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A MATHEMATICAL MODEL FOR A FLUIDIZED-BED COAL GASIFIER

by

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16. ABSTRACT The report gives results of gasifying four fuels--a devolatilized Kentucky bituminous coal, a New Mexico subbituminous coal, a North Carolina peat, and a Texas lignite--with steam and oxygen in a pilot-scale fluidized-bed reactor. Experimental results were used to provide an evaluation of mathematical models developed for the gasifier. A simple three-stage gasifier model and a two-phase bubbling-bed model were developed. Model options include allowance for a jetting region at the gas inlet of the bed and elutriation of fines. Gasification reactions in both models are described by Johnson kinetics. The models were applied to the gasification of the devolatilized Kentucky bituminous coal and the New Mexico subbituminous coal. Parameter optimizations were performed with each model for each feedstock. The main difference in the optimal values was in char reactivity, for which that of the New Mexico coal was roughly an order of magnitude greater than that for the Kentucky char. Using the optimal values, the models were applied to all experimental runs with these two coals. The resulting model predictions and experimental results showed reasonably good agreement in all cases.

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ABSTRACT

A devolatilized Kentucky bituminous coal, a New Mexico subbituminous coal, a North Carolina peat, and a Texas lignite were gasified with steam and oxygen in a pilot-scale fluidized-bed reactor. The reactor was operated at pressures of 570-840 kPa (80-120 psia), molar steam-to-carbon feed ratios of 0.6 to 1.9, and average bed temperatures of 795-1010^{o}C (1460-1850^{o}F). The coal feed rate ranged from 14 to 33 kg/hr (30-73 lb/hr). The experimental results were used to provide a basis for the evaluation of mathematical models of the gasification reactor.

A simple three-stage gasifier model and a two-phase, bubbling-bed gasifier model were developed. The simple model assumes instantaneous devolatilization of coal at the top of the fluidized bed, instantaneous combustion of carbon at the bottom of the bed, and steam/carbon gasification and water gas shift reaction in a single perfectly mixed isothermal stage. The two-phase model is assumed to consist of an incipiently fluidized emulsion phase and a solids-free bubble phase. The solids are assumed to be well-mixed as in the simple model, but plug flow of the gases is assumed. Model options allow for consideration of a jetting region at the gas inlet of the bed and elutriation of fines. The gasification reactions in each model were described by the Johnson kinetics.

The models were applied to the gasification of the devolatilized Kentucky bituminous coal and the New Mexico subbituminous coal. Parameter optimizations were performed with each model for each feedstock. The main difference in the optimal values was in the char reactivity parameter, for which that of the New Mexico coal was roughly an order of magnitude greater than that for the Kentucky char. Using the optimal parameter values, the models were run for all experimental runs. The resulting model predictions and experimental results showed reasonably good agreement in all cases.

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INTRODUCTION

Rising prices and dwindling reserves of natural fuel sources, coupled with readily available reserves of coal, have made coal an increasingly attractive source of energy and chemical feedstocks. For these reasons, much research has centered on such coal conversion processes as pyrolysis, gasification, and liquefaction.

Most research has dealt with optimizing the output of coal conversion processes, while the environmental aspects have received considerably less attention. The U. S. Environmental Protection Agency (EPA), noting this gap in technology, began a study of the environmental consequences of large-scale coal conversion processes. As a part of this study, the EPA contracted for the construction of a coal gasification and gas cleaning pilot plant at North Carolina State University (NCSU). The facility was designed and built by Acurex-Aerotherm Corporation. Design of the gasification reactor, a fluidized-bed unit, was subcontracted to the Institute of Gas Technology. Completed in 1978, the facility is now operated by the faculty, students, and staff of the NCSU Chemical Engineering Department.

The overall objective of the NCSU coal gasification project is to characterize the emissions from the gasification and gas cleaning processes, and to determine how the emission rates of pollutants depend on coal feedstocks and process operating conditions. An important part of this research has been the development of mathematical models of the various gasification and gas cleaning processes. While the overall project objectives include both gasification and gas cleaning, the model development research to be described in this report is concerned only with the gasification process.

The sections that follow will present a review of coal gasification chemistry and gasification modeling, a brief description of the experimental facility, and a presentation of the results of the current work on the modeling of the fluidized-bed gasifier. A complete description of the pilot plant facility and of the experimental data upon which this work is based is given by Ferrell (1980, 1982a, 1982b, 1982c) and Purdy (1983,1984).

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COAL GASIFICATION CHEMISTRY

Coal is a nonhomogeneous material, varying greatly among different coals, and even among different seams of the same coal. To illustrate the differences, Figure 1 shows representative partial structures of several ranks of coal as proposed by Wender (1976). In general, the structure and chemistry of coal are poorly understood, and little fundamental coal knowledge exists. As a result, efforts to describe coal and its chemistry have been largely empirical in nature.

A complex set of reactions occurs in the process of coal gasification with steam and oxygen. The reactions may be divided into the categories of devolatilization, oxidation, gasification, and inorganic reactions. Devolatilization is a very rapid process involving the liberation of volatile coal components and the alteration of the coal structure. The gasification reactions include the reactions of carbon with steam and hydrogen to produce a burnable product gas. Oxidation of carbon to form CO and CO_2 is generally used to provide heat for the gasification reactions. Complete consumption of oxygen is normally achieved. The reactions of inorganic coal components, such as S, N, and trace metals, are primarily of concern for environmental reasons.

DEVOLATILIZATION

Devolatilization, or pyrolysis, is a thermal decomposition of coal to yield tars, liquids, and light hydrocarbons, via a complex set of simultaneous reactions. Figure 2 depicts the devolatilization of a hypothetical coal fragment as proposed by Solomon (Haggin, 1982). In general, an equilibrium yield is rapidly achieved in pyrolysis, which is dependent on the coal type, heating rate, and final temperature. Higher yields are obtained with higher heating rates and higher final temperatures. The amount of tar formed, relative to the gas yield, is decreased at low heating rates, high pressure, and large particle size.

Figures 3-5 presented by Suuberg (1978), show typical devolatilization behavior. Figure 3 indicates that devolatilization occurs rapidly, and in an inert atmosphere (N_2) reaches apparent equilibrium. The slow reaction rate region shown for H_2 atmospheres is probably due to carbon-hydrogen gasification, rather than devolatilization. Figure 4 shows that the yields of all components increase with increasing peak temperature. The effect of pressure is

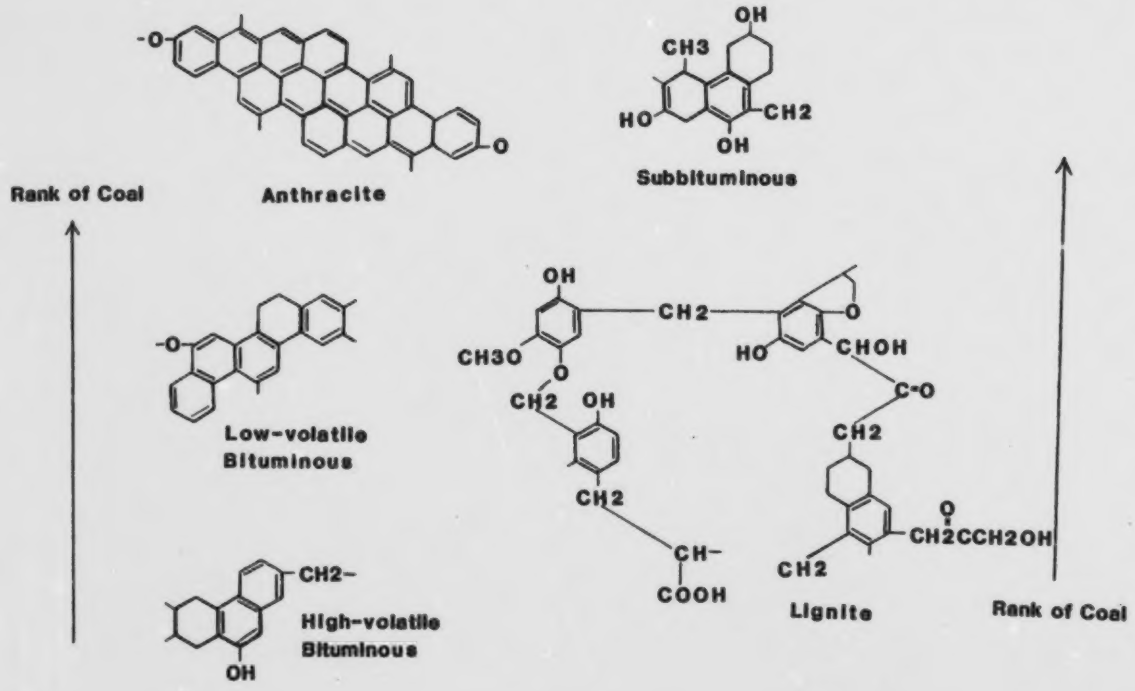
Rank of Coal
Anthracite
Subbituminous
CH3
OH
HO
CH2
OH
Low-volatile Bituminous
High-volatile Bituminous
CH2-
OH
CH3O
CH2
CH2
CH-
COOH
HO
CHOH
C=O
CH2
CH2CCH2OH
O
CH2
Lignite
Rank of Coal

FIGURE I
COAL PARTIAL STRUCTURES

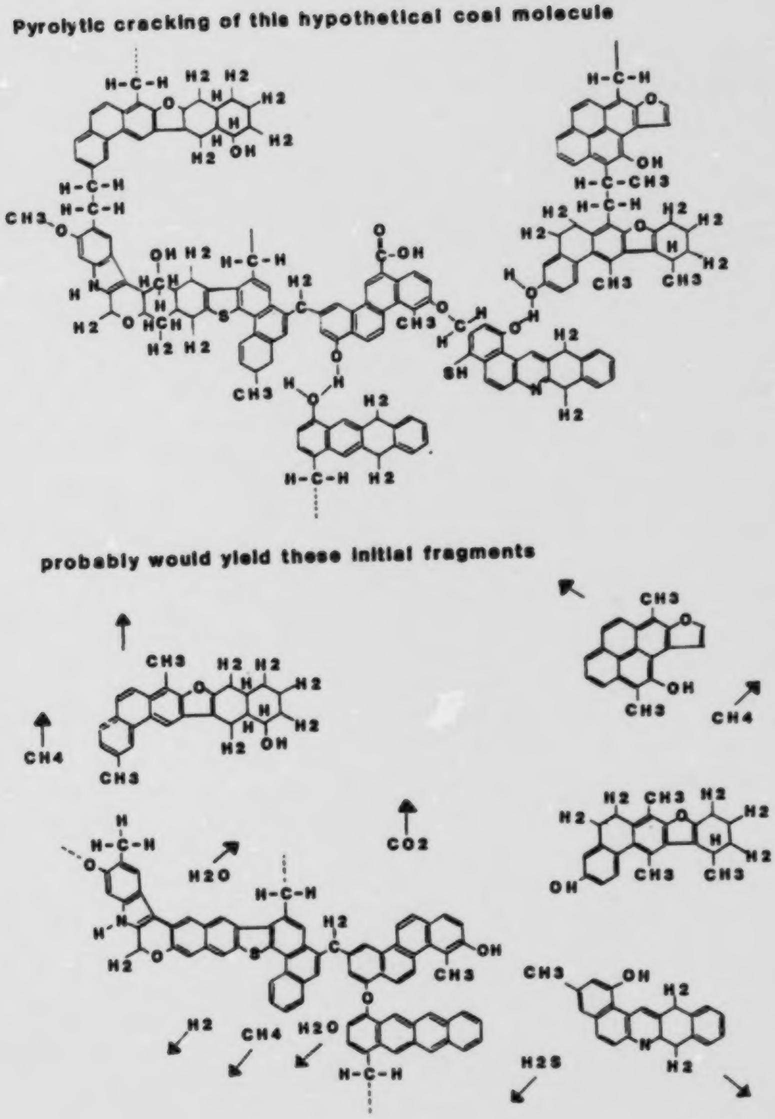
Pyrolytic cracking of this hypothetical coal molecule
probably would yield these initial fragments
CH4
CH4
H2O
CO2
H2
CH4
H2O
H2S

FIGURE 2

SCHEMATIC OF COAL PYROLYSIS

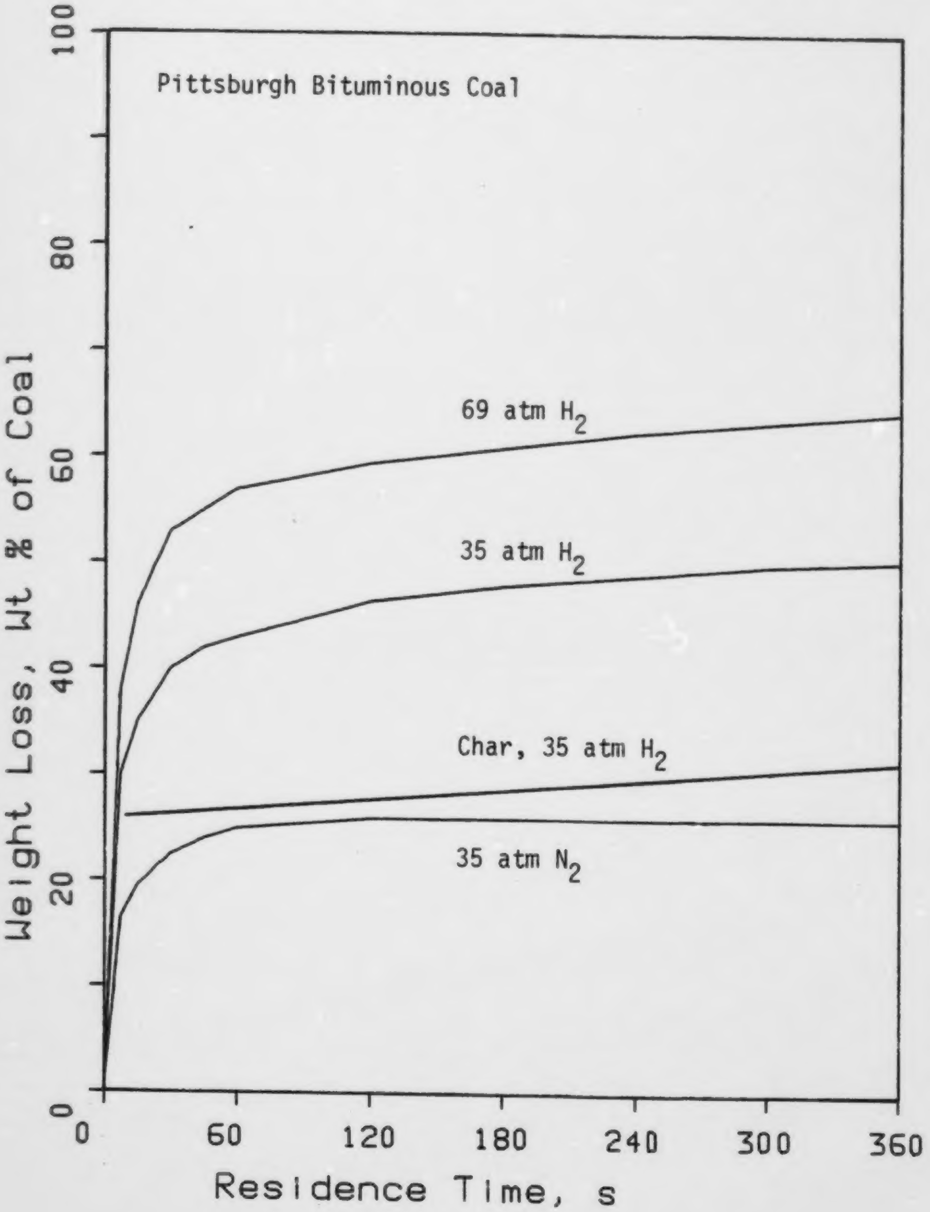

FIGURE 3
EFFECT OF RESIDENCE TIME ON DEVOLATILIZATION YIELDS

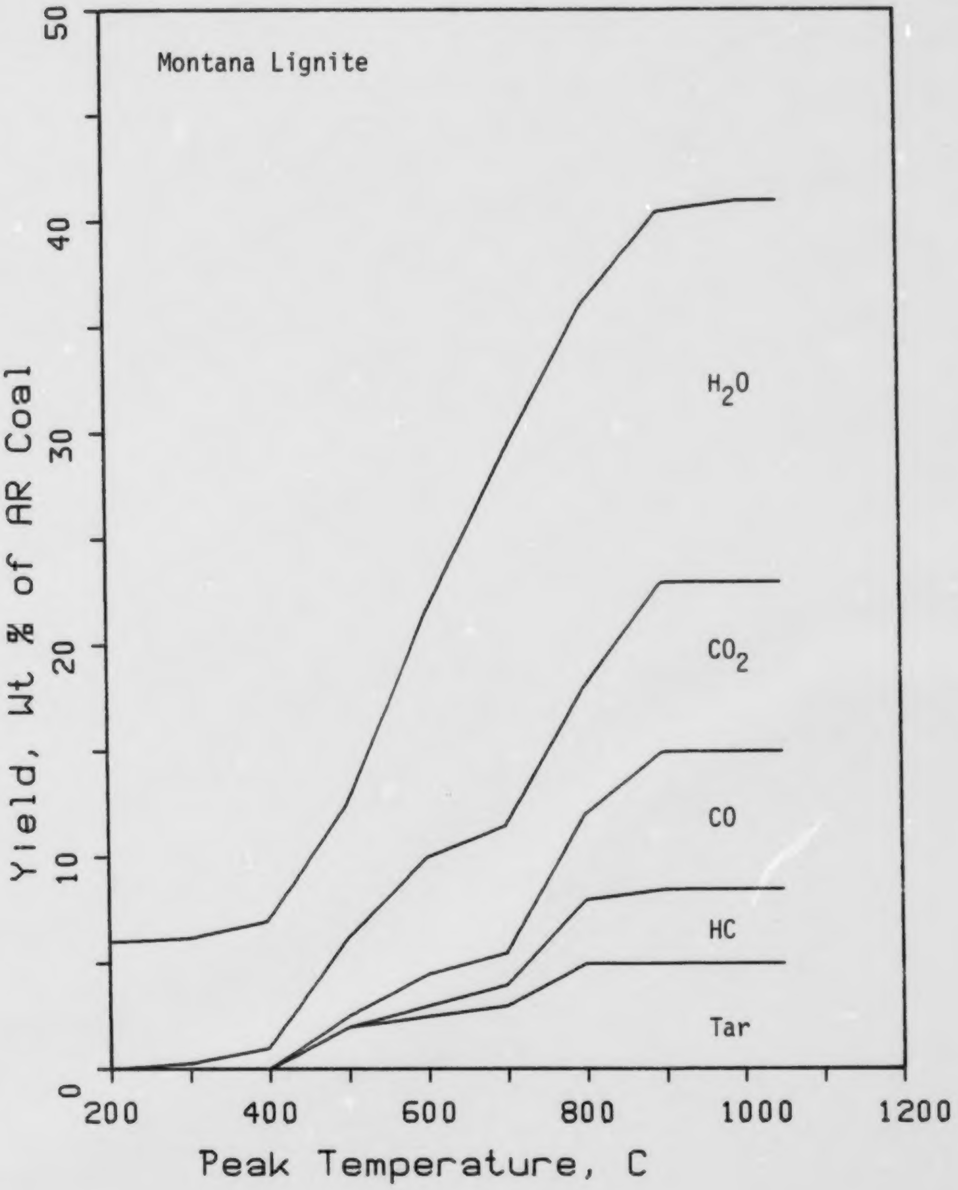

FIGURE 4

EFFECT OF PEAK TEMPERATURE ON DEVOLATILIZATION YIELDS

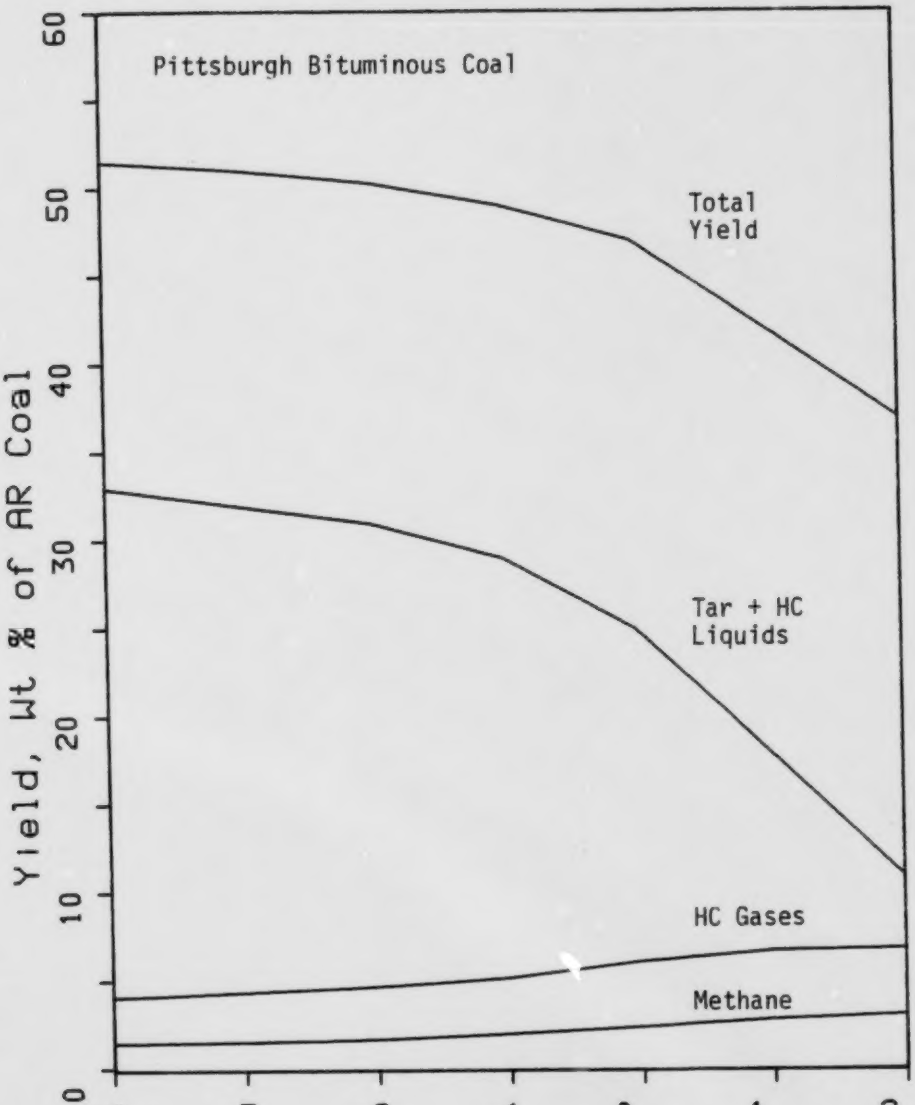

FIGURE 5

EFFECT OF PRESSURE ON DEVOLATILIZATION YIELDS shown in Figure 5 for helium atmospheres. Gas formation is favored by high pressure, while low pressures favor the formation of tars and liquids. The overall devolatilization yield decreases with increasing pressure.

The composition of the gas evolved varies widely. Methane is generally the main product with other light hydrocarbons, CO, CO_2, and H_2 also being evolved. There is generally a tendency to obtain greater amounts of CO and CO_2 at low temperatures.

The kinetics of devolatilization are not well defined, as the process is complex and difficult to analyze. The simplest kinetic expression considered is a first-order expression given by

$$dV/dt = k(V^* - V) \qquad (1)$$

where V = volatile yield
V^* = equilibrium volatile yield

This expression is apparently too simple and has provided inadequate correlation of observed data.

Better results have been achieved using a model that assumes an infinite collection of parallel first-order decomposition reactions, with a normal distribution of activation energies (Anthony, et al., 1975, 1976). The volatiles yield is obtained from this model as

$$\frac{V^* - V}{V^*} = \int_0^\infty \exp[-\int_0^t k_0 \exp\{-E/RT(t)\}dt]F(E)dE \qquad (2)$$

$$F(E) = s^{-1}(2\pi)^{-0.5}\exp[-(E-E_0)^2/2s^2] \qquad (3)$$

where V = volatile yield, wt % (daf)
V^* = equilibrium volatile yield, wt % (daf)
$F(E)$ = activation energy distribution
E_0 = mean activation energy, kcal/mol
k_0 = pre-exponential factor, s^{-1}
s = standard deviation of the activation energy distribution, kcal/mol

Data are correlated by adjustment of the parameters V^*, E_0, k_0, and s.

Table 1 lists parameter values for a lignite and a bituminous coal.

TABLE 1
ANTHONY DEVOLATILIZATION CORRELATION PARAMETERS

	V^*	E_o	k_o	s
Lignite	46.2	56.3	1.67×10^{13}	10.9
Bituminous coal	46.2	54.8	1.67×10^{13}	17.2

The equilibrium volatile yield is an important parameter in Anthony's model and those of other investigators. Kau (1980) fitted the equilibrium fraction dry-ash-free weight loss versus temperature for three coals with a 4th-order polynomial:

$$f = B_0 + B_1T' + B_2(T')^2 + B_3(T')^3 + B_4(T')^4 \qquad (4)$$

where $T'=T(^{o}C)/100$. Table 2 lists the coefficients used to fit data from a batch reactor and a laminar flow reactor.

TABLE 2
WEIGHT LOSS CORRELATION COEFFICIENTS

Coal	B_0	B_1	B_2	B_3	B_4
MRS	-1.783	1.1411	-0.2590	0.02479	-0.0008233
NB8	1.052	-0.7150	0.1615	-0.01367	0.0004044

MRS - Montana Rosebud subbituminous coal
NB8 - North Barber No.8 New Mexico subbituminous coal

Agreda (1979) studied pyrolysis in an equilibrium batch reactor and a laminar flow reactor. Total volatile release and elemental release were measured for five coals. Four models were used to correlate weight loss data for Montana Rosebud subbituminous coal -- Badzioch and Hawksley's (1970) isothermal model, an isothermal 1st-order model, Kobayashi's (1976) nonisothermal 1st-order parallel reactions model, and a nonisothermal 1st-order model. Both nonisothermal models correlated the data well, with the best fit achieved by incorporating temperature-dependent asymptotic weight loss.

Agreda modeled the equilibrium release of the elements As, Se, S, Cl, Pb, and Hg by using the equation

$$f = H(T-T_c)f_e[1 - \exp(-b(T-T_c))] \qquad (5)$$

where f = fractional elemental release
(mass released)/(mass in feed coal)
$H(T-T_c)$ = unit step function
($=0$ for $T-T_c<0$, $=1$ for $T-T_c>0$)
f_e = asymptotic fractional elemental release
T = temperature (^oC)
T_c = critical temperature at which elemental release begins (^oC)
b = empirical constant

The above equation correlated data well for a variety of coals. The following parameter values correlated sulfur data well for a lignite and two bituminous coals: $f_e = 77.1\%$, $T_c = 223^oC$, and $b = 20.08\times10^{-4}\ ^oC^{-1}$.

The kinetics of sulfur release were modeled for a lignite and a subbituminous coal by the 1st-order rate equation

$$\frac{df}{dt} = k_o e^{-E/RT}(f_e - f) \qquad (6)$$

where f is the fractional sulfur release at time t, and f_e is the equilibrium fractional sulfur release. Fitting the equation to experimental results yielded $k_o = 171.113\ s^{-1}$ and $E = 25.02$ kcal/mole.

Suuberg, et al. (1978) used a batch reactor to examine the pyrolysis of a Montana lignite. Volatile yields, expressed as weight percents of the as-received lignite, approached the following values at 1000^oC: 16.5% H_2O, 9.5% CO_2, 9.4% CO, 5.4% tar, 1.3% CH_4, 0.6% C_2H_4, 0.5% H_2, and 0.9% for the sum of ethane, propane, propylene, benzene, and other hydrocarbons. At 1000^oC, 70% of the sulfur and 25% of the nitrogen in the lignite were devolatilized. Product evolution was modeled with sets of independent parallel 1st-order reactions for each species.

Solomon (1977) correlated evolution rates of gases and tar from rapid pyrolysis using a 1st-order rate equation. Temperatures of 300-1250°C and 13 coals (12 bituminous coals and 1 lignite) were used. The rate equation is

$$\frac{dW}{dt} = K_o e^{-E/RT}(W^* - W) \qquad (7)$$

where W is the mass released at any time t and W^* is the equilibrium mass release. The kinetic parameters determined by Solomon are given in Table 3.

TABLE 3
PYROLYSIS KINETIC PARAMETERS - SOLOMON MODEL

Species	K_o s^{-1}	E kcal/mole
H_2	3.6×10^3	25.4
CO_2	33	9.7
CO(1st stage)	7.0×10^3	20.6
CO(2nd stage)	1.1×10^5	34.6
H_2O	27	9.9
Hydrocarbon gases	290	15.9
Tar	81	11.6

The slow pyrolysis of a bituminous coal was studied by Campbell and Stephens (1976), and species evolution was modeled. Data at 110-1000°C were fitted by the equation

$$\frac{dW}{dt} = \frac{K_o W^*}{m} \exp\left[\frac{-E}{RT} - \frac{K_o RT^2}{mE} e^{-E/RT}\right] \qquad (8)$$

where m is the heating rate (dT/dt), W is the mass released at any particular time, and W^* is the equilibrium mass release. Values of K_o and E are given in Table 4.

TABLE 4
PYROLYSIS KINETIC PARAMETERS - CAMPBELL AND STEPHENS MODEL

Species	K_o s^{-1}	E kcal/mole
H_2	20	22.3
CO_2	550	19.5
CO	55	18.0
CH_4	1.67×10^5	31.0
C_2H_4	2.30×10^6	33.4
C_2H_6	1.67×10^6	33.4
C_3H_8	7.30×10^6	35.0

Hydropyrolysis in a batch reactor was examined by Bhatt and Ziegler (1981). For a pulverized North Dakota lignite, the fractional total carbon conversion during hydropyrolysis was correlated as

$$X_C = 1 - [1 + (n-1)k_o \int_0^t \exp(-E/RT)dt]^{1/(1-n)} \qquad (9)$$

By assuming equal activation energies for the postulated reactions, the yields of hydrocarbon gases, benzene, and oils were correlated by

$$\text{Hydrocarbon gases} = (k_1/k_o)X_C \qquad (10)$$

$$\text{Benzene} = (k_2/k_o)X_C \qquad (11)$$

$$\text{Oils} = (k_3/k_o)X_C \qquad (12)$$

Data fitting yielded the following parameter values: $n=6$, $E=205$ kJ/mole, $k_o=9.95 \times 10^9$, $k_1=2.72 \times 10^9$, $k_2=0.18 \times 10^9$, and $k_3 = 7.05 \times 10^9$ (all k values in s^{-1}).

Rapid devolatilization in transport reactors was studied by Friedman et al.(1968) and Eddinger et al.(1966). The short residence time reactors achieved heating rates as high as 1200°C/s. The coals utilized were a Wyoming subbituminous coal, an Illinois bituminous coal, and two West Virginia bituminous coals. The product distributions were measured for a series of devolatilization conditions. Temperature, residence time, and the carrier gas were the main variables examined. A major focus of the work was the maximization of tar yields, which was achieved with helium carrier gas, moderate temperatures of around 600°C, and residence times of 0.5 to 2.0 s.

A different approach to pyrolysis modeling has been taken by Solomon (1979) and Gavalas et al. (1981). Both represented coal as a collection of various functional groups, with each functional group having reaction rate constants independent of coal type. The distribution of functional groups determines the differences between various coals.

Solomon used 10 functional groups in his model. Experimentally, the functional group concentrations were determined from ultimate analysis and infrared spectroscopy data. Tars are formed by the release of large coal fragments ("monomers") from the coal "polymer" structure, and lighter species result from cracking reactions. The model gave results which compared reasonably well with data for a Pittsburgh seam bituminous coal and a Montana lignite.

The model of Gavalas includes 14 functional groups and 42 elementary reactions. The chosen reactions were based on the expected chemical transformations in the temperature range of interest, 400-700°C. Isothermal particles were assumed, which is valid for particles under 0.5mm and heating rates of 1000°C/s or less. Mass transfer effects in macropores were neglected, and an empirical factor was introduced to account for diffusion resistances in the coal phase. Good comparisons with data for a subbituminous coal and a bituminous coal were obtained. The functional group distributions for the two coals were determined from ultimate analysis and nuclear magnetic resonance data.

OXIDATION

The oxidation of carbon to form CO and CO_2 is an important part of most gasification schemes currently under consideration, as the reaction is used to provide heat for the endothermic carbon-steam reaction. The following basic steps are usually accepted as being part of the reaction mechanism: diffusion of oxygen to the coal surface, surface reaction, desorption of CO or CO_2, and diffusion back into the bulk gas stream. Consideration of all steps leads to a complex rate expression with many constants to be determined. The problem is eased if one step may be considered limiting. The final rate expression then depends on the rate of the limiting step.

Parker and Hottel (1936) studied the oxidation of brush carbon in an atmospheric reactor and temperatures of 680-960°C.They determined that the carbon oxidation rate was inversely proportional to the sum of diffusional and chemical resistances. The correlation is

$$r(g/cm^2 s) = p_{O2}/(R_d + R_c) \qquad (13)$$

where p_{O2} is the oxygen partial pressure in atm, R_d is the diffusional resistance, and R_c is the chemical resistance. R_d and R_c are given as

$$R_d = [3.2\times10^{-5}T^{0.5}AP(117(dup)^{0.37}/dT^{0.185} + 2/d)]^{-1} \qquad (14)$$

$$R_c = 1.05\times10^{-7}T^{0.5}\exp(44000/RT) \qquad (15)$$

T = temperature of carbon surface, ^oK
P = total pressure, atm
d = particle diameter, cm
u = gas velocity, cm/s
p = gas density, g/cm^3
A = function of pressure and gas diffusivities, for air at 1 atm, A=0.168 $cm^2atm^{-1}s^{-1}$

Hsia and Edgar (1978) developed a model for the oxidation of Texas lignite char. In the range 330-440 ^oC and oxygen partial pressures of 0.25 to 1.5 atm, the rate of carbon combustion by oxidation was correlated by

$$dX/dt = (AP_{O2}/(1+BP_{O2}))\exp(-E_a/RT) \qquad (16)$$

where A, B, and E_a are constants. For Texas lignite, the following values were obtained: $A=2.3\times10^8$, B=0.655, and E_a=34.1 kcal/mole. The effective reaction order with respect to oxygen partial pressure varies from zero to one.

Field, et al (1967) found a first-order rate expression for temperatures of 700 to 1400 ^oC, under conditions where mass transfer resistance is negligible:

$$r(g/cm^2s) = 8.71\times10^3P_{O2}\exp(-E/RT) \qquad (17)$$

with P_{O2} in atmospheres and E=35.7 kcal/mole.

Generally, however, the rate of oxidation is not of great importance in modeling since the reaction is extremely rapid and is assumed to proceed to complete oxygen conversion. Thus, the amount of O_2 available, not the reaction rate, determines the extent of oxidation. Of greater importance are the relative amounts of CO and CO_2 formed by reaction.

It has been suggested that the oxidation stoichiometry can be described by the equation

$$C + aO_2 = (2-2a)CO + (2a-1)CO_2 \tag{18}$$

where a is a temperature-dependent function (Arthur, 1951). Arthur found that in the range 460-900 ^{o}C, a could be expressed as

$$a = 0.5 \left[\frac{2+10^{3.4}\exp(-E/RT)}{1+10^{3.4}\exp(-E/RT)} \right] \tag{19}$$

where T is in degrees Kelvin and E=12.4 kcal/mole. This can be rearranged to give the CO/CO_2 product ratio as

$$CO/CO_2 = 10^{3.4}\exp(-E/RT) \tag{20}$$

However, the conditions for which a was determined differ from the actual conditions in a gasifier; thus the general applicability of this expression is questionable.

Phillips, et al.(1970) performed a similar study to determine the CO/CO_2 production distribution from combustion. An exponential correlation, similar to Arthur's, was used. The correlation is given by

$$CO/CO_2 = A\exp(-E/RT) \tag{21}$$

where E = 6.4 kcal/mol. The preexponential factor A was found to be highly dependent on the fractional carbon burnoff and the surface oxide concentration. The widely varying A factor found by Phillips and the differing activation energies found by Arthur and Phillips suggest that in some cases it may be best to leave the CO/CO_2 distribution factor as an adjustable model parameter.

A combustion zone can be defined as the region of the bed where combustion occurs, or the region where the O_2 concentration is not zero. For typical O_2 flow rates, the combustion zone is very small, and is often assumed to have negligible thickness. This assumption is convenient for modeling.

Sundaresan and Amundson (1979b) tested the validity of the negligible combustion zone thickness assumption. Their results indicated that the assumption is good for most cases encountered in coal gasification. The assumption is best at low O_2 feed rates, high solids residence times, and high pressures.

GASIFICATION REACTIONS

The primary goal of coal gasification is the conversion of solid coal to a clean burning fuel gas. This is primarily achieved by carbon conversion to CO and CH_4, and simultaneous reduction of steam to form H_2. The exact mechanisms of steam gasification are not well known; however, several kinetic studies have yielded rate correlations. The following reactions are generally considered in gasification:

$C + H_2O = CO + H_2$ (steam gasification) (22)
$C + 2H_2 = CH_4$ (hydrogasification) (23)
$CO + H_2O = CO_2 + H_2$ (shift reaction) (24)

Pulsifer (1976) investigated the steam gasification of a bituminous coal and two coal chars in a fixed bed reactor. For pressures of 1 to 41 bars and temperatures of 600 to 1100 °C, the rate of carbon conversion was correlated by

$$dX/dt = [AP_{H2O}/(1+BP_{H2O})](1-X) \tag{25}$$

where A and B follow Arrhenius type temperature dependencies. For a German bituminous coal the following were obtained:

$$A = 1.88x10^{6}exp(-2.24x10^{4}/T(K)) \tag{26}$$
$$B = 1.56x10^{-5}exp(-1.65x10^{4}/T(K)) \tag{27}$$

with A in $min^{-1}atm$, and B in atm^{-1}. The expressions for A and B are dependent on the material being gasified.

A somewhat different expression for the rate of steam gasification was developed by Wen (1972), who found Langmuir-type expressions inconvenient in optimization studies. Wen found that the rate, expressed as moles of carbon reacting per mole present, could be given by

$$r = k_v(y_{H2O} - RTy_{H2O}y_{CO}/K) \tag{28}$$

where K is an equilibrium constant, y's are gas phase mole fractions, and k_v is a rate constant evaluated for various conditions by Wen.

Sundaresan and Amundson (1979a) present correlations for the kinetics of char gasification proposed by Gibson and Euker. Steam gasification, hydrogasification, and the shift reaction are considered, with the shift reaction assumed to be at equilibrium. The rate of carbon conversion is given by

$$dX/dt = f_o(1-X)[k_{o1}(P_{H2O}-P_{CO}P_{H2}/K_1) + k_{o2}(P_{H2}-P_{CH4}{}^{0.5}/K_2)] \tag{29}$$

f_o = char reactivity, property of char
k_{o1}, k_{o2} = Arrhenius type rate constants

For an Illinois coal, k_{o1} and k_{o2} in $atm^{-1}sec^{-1}$ are given by

$$k_{o1} = 625.83\exp(-21200/T) \tag{30}$$
$$k_{o2} = 0.33\exp(-10760/T) \tag{31}$$

where T is in ^{o}K, while for a Wyoming coal

$$k_{o1} = 1226.4\exp(-18780/T) \tag{32}$$

K_1 and K_2 are equilibrium constants for the carbon-steam and carbon-hydrogen reactions, and given by the following expressions where T is in ^{o}K:

$$\log_{10}K_1 = 7.49 - 7070/T \tag{33}$$
$$\log_{10}K_2 = -5.373 + 4723/T \tag{34}$$

This model is one of the simplest that is thermodynamically consistent.

Probably the most prominent coal gasification kinetics correlation is that developed by Johnson (1974) of the Institute of Gas Technology (IGT). Johnson used a high pressure thermobalance to study a variety of coals. The rate of carbon conversion in char gasification, expressed as fraction carbon consumed per minute, was correlated by

$$dX/dt = f_L k_T (1-X)^{2/3} \exp(-bX^2) \tag{35}$$

where f_L is a relative reactivity factor, X is the fractional base carbon conversion, and b is a kinetic parameter dependent on pressure and gas composition. The relative reactivity factor is defined by

$$f_L = f_o \exp(8467/T_p) \tag{36}$$

f_o = reactivity factor which is a property of the coal char
T_p = pretreatment temperature, ^oR
T = gasification temperature, ^oR
(if $T > T_p$, then $T_p = T$)

k_T is the sum of individual rate constants for three reactions, which are complex functions of partial pressures and temperature. The reactions are

$$C + H_2O = CO + H_2 \tag{37}$$
$$C + 2H_2 = CH_4 \tag{38}$$
$$2C + H_2 + H_2O = CO + CH_4 \tag{39}$$

It should be noted that reaction 39 is the sum of reactions 37 and 38. The Johnson kinetic parameters are summarized in Table 5.

SHIFT REACTION

The water gas shift reaction,

$$H_2O + CO = CO_2 + H_2 \tag{40}$$

TABLE 5

JOHNSON KINETIC PARAMETERS

$$k_1 = \frac{\exp(9.0201 - 31705/T)\left(1 - \frac{P_{CO}P_{H2}}{P_{H2O}K_1}\right)}{\left[1 + \exp(-22.216+44787/T)\left(\frac{1}{P_{H2O}} + 16.35\frac{P_{H2}}{P_{H2O}} + 43.5\frac{P_{CO}}{P_{H2O}}\right)\right]^2}$$

$$k_2 = \frac{P_{H2}{}^2\exp(2.6741 - 33076/T)\left(1 - \frac{P_{CH4}}{P_{H2}{}^2K_2}\right)}{1 + P_{H2}\exp(-10.4520 + 19976/T)}$$

$$k_3 = \frac{P_{H2}{}^{0.5}P_{H2O}\exp(12.4463 - 44544/T)\left(1 - \frac{P_{CH4}P_{CO}}{P_{H2}P_{H2O}K_3}\right)}{[1 + \exp(-6.6696 + 15198/T)(P_{H2}{}^{0.5} + 0.85P_{CO} + 18.62P_{CH4}/P_{H2})]^2}$$

$$b = \frac{52.7P_{H2}}{1 + 54.3P_{H2}} + \frac{0.521P_{H2}{}^{0.5}P_{H2O}}{1 + 0.707P_{H2O} + 0.50P_{H2}{}^{0.5}P_{H2O}}$$

P_i = partial pressure of component i, atm
T = temperature, ^{o}R
k_1, k_2, k_3 = equilibrium constants

---

is an important reaction in gasification. The reaction is thought to occur on the char surface; thus, Langmuir-Hinshelwood rate expressions have been proposed for it. Wen and Tseng (1979), however, have presented a simpler rate expression:

$$r = f_{wg}kP[y_{CO} - y_{H2}y_{CO2}/(y_{H2O}K)] \qquad (41)$$

r = rate in gmole/cm^{3}s
f_{wg} = shift reactivity parameter, dependent on char
P = total pressure, atm
K = equilibrium constant
k = rate constant, given by
$k = 1.26\text{x}10^5\exp(-E/RT)$,
with E = 27.76 kcal/mol

The above rate equation describes the shift reaction when it is catalyzed by a solid surface. The homogeneous uncatalyzed shift reaction rate has been described by Karim and Mohindra (1974) with the following rate expression:

$$r = 2.864\text{x}10^{15}\exp(-E/RT)\rho_g{}^2(y_{CO}y_{H2O} - y_{CO2}y_{H2}/K_{eq})$$

r = reaction rate, lbmole/(ft^{3}min)
E = activation energy = 88200 cal/gmol
R = gas constant
T = temperature
ρ_g = gas density, lbmole/ft^3
y_i = gas mole fractions
K_{eq} = shift reaction equilibrium constant

A rate expression similar to equation (42) was used by Biba, et al.(1978) in their fixed-bed gasification modeling. The kinetic parameters that they used -- a pre-exponential factor of 2.671x10^6 ft^3/lbmole/min and an activation energy of 3003 cal/gmol -- were much different than those of Karim and Mohindra.

It has often been assumed that the shift reaction is at equilibrium during gasification processes and that rate expressions do not have to be considered. However, the validity of the assumption is questionable, especially at low pressures.

INORGANIC REACTIONS

The reactions of inorganic coal constituents are of interest mainly because of environmental considerations. Gasification produces a number of byproducts which may be toxic, odorous, or unacceptable in further processing steps. Volatile trace metals such as lead, mercury, arsenic, etc., can be highly toxic. Nitrogen can react to form ammonia, cyanides, cyanates, and thiocyanates. The most abundant of the inorganic constituents, sulfur, reacts in char gasification to yield primarily H_2S and COS. Carbon disulfide, mercaptans, and thiophenes may also be formed, particularly during devolatilization.

The kinetics of sulfur reactions during gasification are not well understood. Generally sulfur in coal is broken into three classes -- sulfate, pyritic, and organic -- with reaction kinetics differing for each form of sulfur. Organic sulfur is often broken into 3 subclasses of differing reactivities -- Organic I, Organic II, and Organic III -- each with progressively greater stability.

The devolatilization of sulfur was studied by Solomon (1977). A 1st-order rate expression was used to correlate sulfur release. The frequency factors and activation energies determined by Solomon for 12 bituminous coals and a lignite are given in Table 6.

TABLE 6
PYROLYSIS KINETIC PARAMETERS FOR SULFUR - SOLOMON MODEL

Form of Sulfur	Frequency factor s^{-1}	Activation energy kcal/mole
Pyritic	600	16.7
Organic I	100	11.6
Organic II	10	11.6
Organic III	2.2×10^9	56.1

Yergey et al. (1974) and Vestal et al. (1972) studied sulfur reactions in hydrogen atmospheres using nonisothermal kinetic methods. The following reactions were studied:

$$\text{Organic I} + H_2 = H_2S \quad (43)$$
$$\text{Organic II} + H_2 = H_2S \quad (44)$$
$$\text{Organic III} + H_2 = H_2S \quad (45)$$
$$FeS_2 + H_2 = H_2S + FeS \quad (46)$$
$$FeS + H_2 = H_2S + Fe \quad (47)$$

$$Fe(s) + H_2S = FeS + H_2 \quad (48)$$
$$C(s) + H_2S = H_2S(\text{adsorbed}) \quad (49)$$
$$CaO(s) + H_2S = CaS + H_2O \quad (50)$$

Rate expressions are of the form

$$-\frac{d[A_j\text{-}S]}{dt} = \left(\frac{d[H_2S]}{dt}\right)_j = k_{o,j}e^{-E/RT}[H_2][A_j\text{-}S]^n \quad (51)$$

for reactions 43-47, and

$$-\frac{d[H_2S]}{dt} = k_{o,j}e^{-E/RT}[H_2S] \quad (52)$$

for reactions 48-50. $[H_2]$ and $[H_2S]$ are gas phase concentrations, while $[A_j\text{-}S]$ represents the concentration of solid sulfur bound to site A_j. The kinetic parameters are summarized in Table 7. The apparent parameters were determined by neglecting the back reactions (48-50). The true parameters were obtained after consideration of the effect of the back reactions on measured H_2S production rates.

TABLE 7
SULFUR REACTION KINETIC PARAMETERS

Rxn	Rxn order with respect to sulfur species	Apparent E	Apparent k_o	True E	True k_o
43	1	34.5	3.1×10^{10}	---	---
44	1	41.5	2.8×10^{11}	---	---
45	2	38.1	2.5×10^{7}	56.1	1.3×10^{11}
46	0.5	42.1	1.3×10^{11}	42.1	1.3×10^{11}
47	1	25.1	1.8×10^{5}	43.1	9.7×10^{8}
48	1	---	---	18.0	6.5×10^{4}
49	1	---	---	32.0	2.3×10^{8}
50	1	---	---	38.0	4.7×10^{13}

units of E are kcal/mole; units of k_o are $(\text{atm } H_2)^{-1}\text{min}^{-1}$ for reactions 43-47, $(\text{atm } H_2S)^{-1}\text{min}^{-1}$ for reactions 48-50

The given expressions are probably oversimplified and inadequate for many conditions; however, they are as good as any existing correlations.

It is likely that the sulfate and pyrite forms of sulfur are depleted during pyrolysis, leaving sulfide and organic as the primary forms of sulfur. Figure 6, taken from Vestal, et al.(1969), shows a H_2S evolution curve for a Kentucky coal processed in one atmosphere of hydrogen. The plot resolves the overall evolution of H_2S into separate processes, each representing the breakdown of a particular form of sulfur in the coal. It can be seen that the Organic I and II and pyrite sulfur form reactions are complete by 550°C, a relatively low temperature ordinarily achieved in the pyrolysis stage of coal gasification. Figure 7 (Vestal et al., 1969) shows the variation of sulfur forms versus temperature for an Illinois coal processed under similar conditions. Above 550°C the coal sulfur is essentially comprised of only the sulfide and organic forms, with negligible quantities of sulfate sulfur present. Based on Figures 6 and 7, it might be assumed that pyrolysis converts coal sulfur to the sulfide and organic forms, with the organic fraction being largely of the Organic III class.

Once the sulfur has been converted into a gaseous form, gas phase reactions may occur. It is thought that COS is formed from the following gas phase reactions

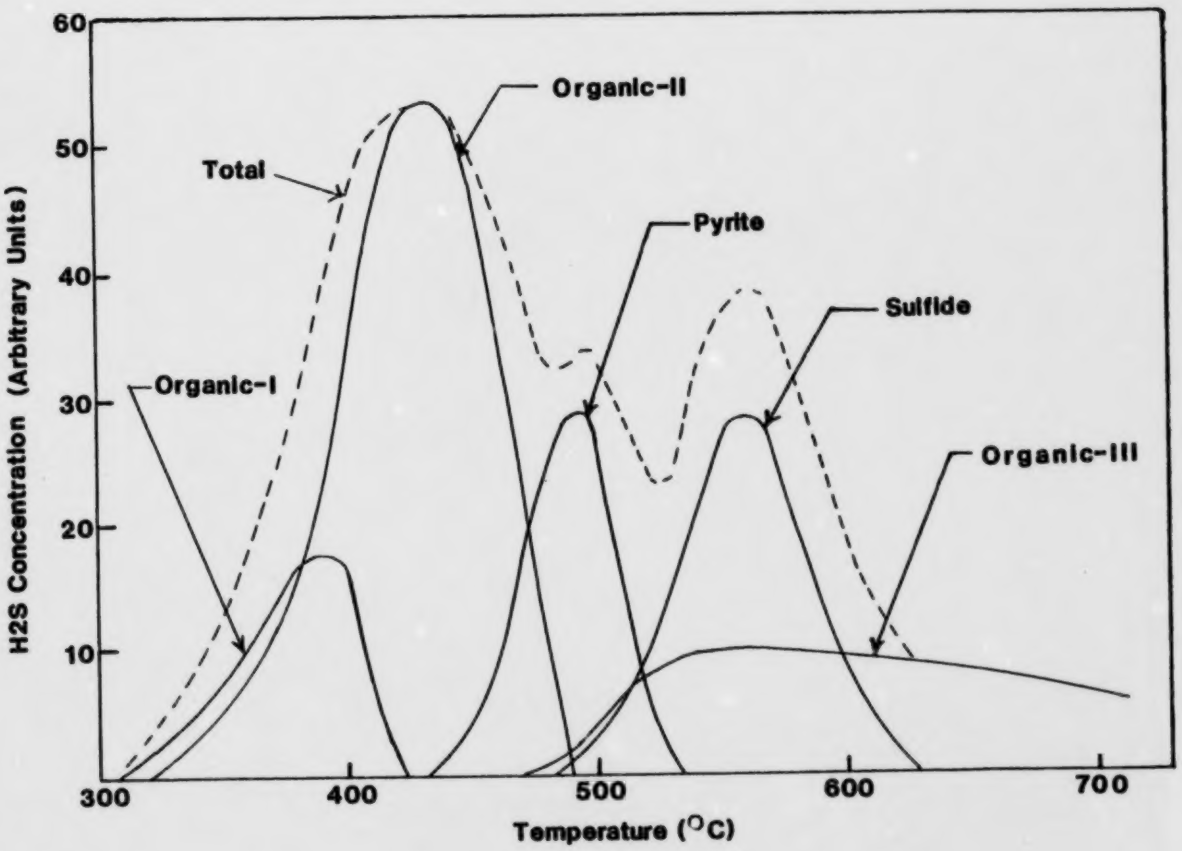

FIGURE 6

HYDROGEN SULFIDE EVOLUTION VERSUS TEMPERATURE

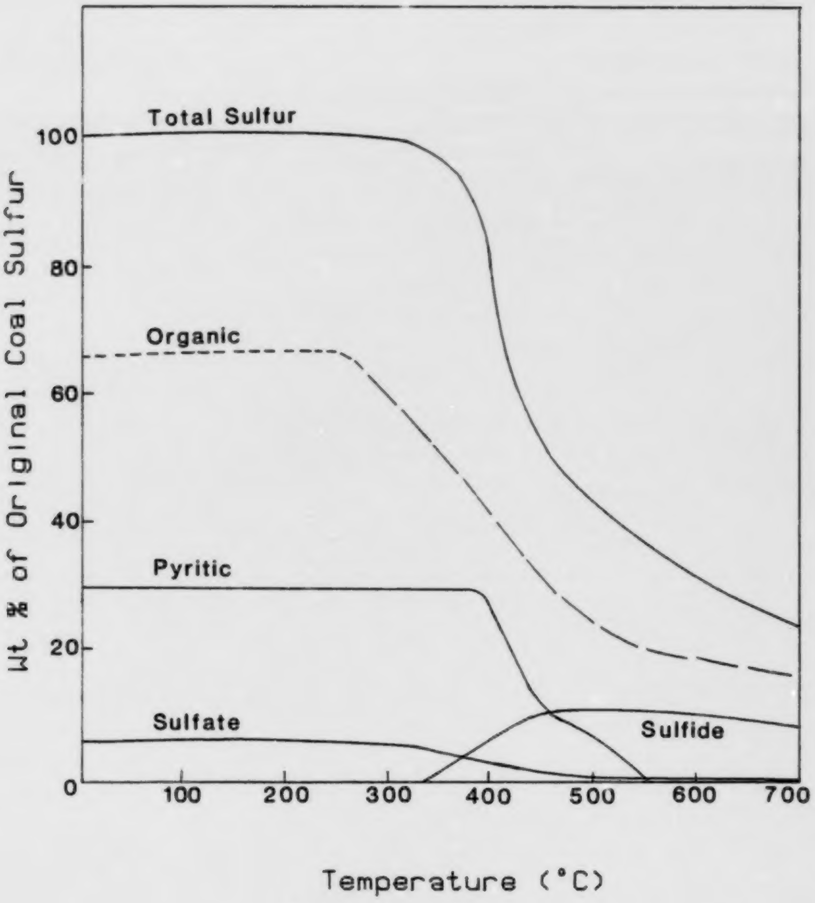

FIGURE 7
EFFECT OF TEMPERATURE ON SULFUR DISTRIBUTION

$$H_2S + CO_2 = COS + H_2O \tag{53}$$

$$H_2S + CO = COS + H_2 \tag{54}$$

Equilibrium data for these reactions presented by Kohl and Riesenfeld (1979) are given in Table 8.

TABLE 8
SULFUR REACTION EQUILIBRIUM DATA

T °C	$K_1 = \frac{[H_2S][CO_2]}{[COS][H_2O]}$	T °C	$K_2 = \frac{[H_2S][CO]}{[COS][H_2]}$
20	7.25×10^5	227	7.55
100	3.16×10^4	327	10.9
200	2.75×10^3	427	13.8
300	5.55×10^2	527	16.0
400	1.85×10^2	627	17.8
500	81.0	727	19.0
600	43.1		
700	26.1		
800	17.3		
900	12.3		
1000	4.5		

The above data have been well fitted by the equations

$$\ln K_1 = -1.352 + 7881.61/T \tag{55}$$
$$\ln K_2 = 3.395 - 610.212/T \tag{56}$$

where T is the temperature in °R.

Nitrogen gases found in gasifier effluents consist mainly of NH_3 and HCN, along with lesser amounts of thiocyanates, molecular nitrogen, and nitrogen oxides. In devolatilization, the primary products are NH_3 and HCN. Measurements of coking operations have indicated that NH_3 is the main product, while other studies (Blair, et al., 1977; Sharkey, et al., 1966; and Bond, et al., 1966) have determined that HCN is the main nitrogen product. Klein and Juntgen (1972) found that greater releases of fuel nitrogen are attained at increasing temperatures, and that lesser releases are obtained for increasing coal rank. Solomon (1977) postulated a 1st-order rate expression for nitrogen release. A frequency factor of 3.6 s^{-1} and an activation energy of 15.0 kcal/mole were used to correlate pyrolysis data for 12 bituminous coals and a lignite.

In gasification, fuel nitrogen is generally converted to a slightly greater extent than carbon, with NH_3 being the main product (Smoot and Pratt, 1979). Further reaction of NH_3 with carbon to form HCN is possible. Small quantities of nitrogen oxides such as NO, NO_2, and N_2O are formed in the combustion zone of gasifiers. The oxides may result from fixation of feed N_2, or more likely from reactions of the fuel nitrogen.

FLUIDIZED-BED MODELING

A wide variety of models have been applied to fluidized-beds. Initial efforts were modifications of the dispersion model, where dispersion coefficients may vary from zero for plug flow to infinity for perfect mixing. The dispersion model, along with others such as single tanks and tanks-in-series models, has generally been inadequate in modeling fluidized-bed processes.

Multi-phase models were proposed as an improvement in fluidized-bed modeling. Two-phase models, consisting of emulsion and bubble phases, were first developed in the 1950's. The continuous emulsion phase is a gas-solid mixture, and is generally assumed to be at minimum fluidization conditions. The bubble phase is commonly assumed to consist of particle-free gas that passes through the bed in plug flow. Further developments have added cloud and wake phases. The cloud phase is the boundary region separating the bubble and emulsion, while the wake phase consists of particles carried upward by the bubble. Using this framework, a large number of multi-phase models have been applied to various fluidization processes. The bulk of the variations have dealt with describing intra- and inter-phase mass transport.

Despite their differences, there are many features common to most multi-phase models. The following sections briefly detail some of the equations and correlations that are used to describe the common features of fluidized-bed reactor models.

FLUIDIZATION PARAMETERS

Minimum Fluidization Velocity

The minimum fluidization velocity, u_{mf}, is the minimum gas velocity to incipiently fluidize a bed. The correlation suggested by the IGT Coal Conversion Technical Data Book (1978) for coal and related materials is:

$$u_{mf} = \frac{v}{p_g d_p} \left[[(25.25)^2 + 0.0651Ar]^{0.5} - 25.25 \right] \qquad (57)$$

where Ar is the Archimedes number, defined by

$$Ar = \frac{p_g(p_s - p_g)gd_p^3}{v^2} \tag{58}$$

v = gas viscosity (kg/m-s)
p_g = gas density (kg/m^3)
p_s = solids density (")
d_p = average particle diameter (m)
g = acceleration of gravity (m/s^2)

An alternate correlation strictly for coal char was presented by Wen (1972). The correlation is

$$\frac{u_{mf}p_g d_p}{v} = 0.0135(Ar)^{0.73} \tag{59}$$

The terms in the correlation are defined in the same manner as for equations (57) and (58).

Bed Expansion

The bed expansion factor is the ratio of the actual height of a fluid bed to the height if it were minimally fluidized. The gas in excess of the minimum causes an expansion of the bed height. The ratio can be estimated from the following correlation given by IGT (1978):

$$B = H/H_{mf} = 1.0 + \frac{10.978(u_o - u_{mf})^{0.738}p_s^{0.376}d_p^{1.006}}{u_{mf}^{0.937}p_g^{0.126}} \tag{60}$$

B = bed expansion factor
H = actual bed height, m
H_{mf} = height at minimum fluidization conditions, m
u_o = gas velocity, ft/s
u_{mf} = minimum fluid. velocity, ft/s
p_g,p_s = gas and solid densities, lb/ft^3
d_p = average particle diameter, ft

The gas velocity is the total volumetric gas flow rate, calculated at the bed temperature and pressure, divided by the bed cross-sectional area.

Bubble Parameters

The volume fraction of the fluidized bed occupied by bubbles is calculated from the bed expansion factor as

$$b = (H - H_{mf})/H = (B - 1)/B \qquad (61)$$

The bubble velocity can then be calculated from a gas mass balance:

$$u_b = \frac{u_o - (1 - b)e_{mf}u_e}{b} \qquad (62)$$

u_b = bubble velocity, m/s
e_{mf} = emulsion phase voidage at minimum fluidization (void space/total space)
u_e = emulsion gas velocity, m/s
u_s = solids velocity, m/s

Correlations to predict the bubble velocity are also available.

Several correlations for predicting bubble diameter have been developed. The correlations to follow require all terms to be in units of g, cm, and s. Kato and Wen (1969) proposed the following equation for determining the bubble diameter:

$$d_b = d_o + 1.4p_p d_p(u/u_{mf})h \qquad (63)$$

where h is the height above the gas distributor and d_o is the initial bubble diameter at the distributor.

A correlation was developed by Mori and Wen (1975) for freely bubbling fluidized-beds. The correlation is

$$\frac{d_{bm} - d_b}{d_{bm} - d_o} = \exp(-0.3h/d_c) \tag{64}$$

where d_{bm} is the maximum bubble diameter due to coalescence, and d_c is the bed diameter. The maximum bubble diameter is given by

$$d_{bm} = 0.652[A(u - u_{mf})]^{0.4} \tag{65}$$

The initial bubble diameter for a perforated plate distributor can be calculated by the following equation suggested by Kato and Wen (1969):

$$d_o = \left(\frac{6A(u - u_{mf})}{ng^{0.5}}\right)^{0.4} \tag{66}$$

or by the Mori and Wen (1975) equation:

$$d_o = 0.347[A(u-u_{mf})/n]^{0.4} \tag{67}$$

where A is the distributor area, and n is the number of orifices in the distributor. For a porous plate distributor Mori and Wen recommend the equation

$$d_o = 0.00376(u - u_{mf})^2 \tag{68}$$

Solids Circulation

In a fluidized-bed the solid particles are constantly circulated by the uprising gas flow. The circulation rate, or turnover rate, at any point in the bed can be estimated by the correlation of Talmor and Benenati (1963).

$$W = 49.0(u_o - u_{mf})\exp(-2021d_p) \qquad (69)$$

W = turnover rate, lb/(ft^{2}s)
u_o, u_{mf} = velocities, ft/s
d_p = avg particle diameter, ft

Particle Size Reduction

Coal particles in a fluidized-bed undergo size reduction as a consequence of particle-particle and particle-wall abrasion. Merrick and Highley (1974) studied particle size reduction for fluidized-beds of coal ash, and developed the correlation

$$\frac{dx}{dt} = -k_a f_x(u - u_{mf})x \qquad (70)$$

x = particle size, m
k_a = abrasion constant, m^{-1}
f_x = fraction of particles in the bed smaller than size x
u = gas velocity, m/s
u_{mf} = minimum fluidization velocity, m/s

The abrasion constant, k_a, is a function of the bed solids, and reflects the friability of that material. The term f_x is assumed to equal the fraction of the time that a particle undergoes abrasion. Small particles, having small f_x values, spend greater amounts of time in void volumes, and thus experience less abrasion.

Elutriation

Elutriation from a fluidized-bed is generally described by equations of the form

$$R_x = E_x b_x \tag{71}$$

where R_x is the elutriation rate of particles of size x, E_x is the elutriation rate constant for particles of size x, and b_x is the weight fraction of particles of size x in the bed. The total elutriation rate is given by the summation of the R_x:

$$R = \quad R_x = \quad E_x b_x \tag{72}$$

The elutriation rate constants are primarily functions of the fluidizing gas, the gas velocity, and particle size and density.

Merrick and Highley (1974) developed the following correlation from their studies of coal ash elutriation from the British Coal Utilization Board's pilot-scale coal combustor.

$$\frac{E_x}{G} = A + 130\exp\left[-10.4\left(\frac{u_t}{u_o}\right)^{0.5}\left(\frac{u_{mf}}{u_o - u_{mf}}\right)^{0.25}\right] \tag{73}$$

G = mass velocity of fluidizing gas, kg/m^{2}s
u_t = terminal velocity of particles of size x, m/s
u_o = actual gas velocity, m/s
u_{mf} = minimum fluidization velocity, m/s

The parameter A is the minimum E_x/G value, which is a function of the fluidized bed vessel. For the British Coal Utitilization Board's pilot scale coal combustor, A was generally found to be of little importance. (In the modeling studies that follow, it is assumed that A=0 for the NC State gasifier.)

Wen and Chen (1982) studied entrainment and elutriation from fluidized beds. At sufficient gas flow rates, solids are entrained by the drag force of the gas. The entrainment rate generally decreases with increasing height above the bed surface. At some height above the bed the entrainment rate undergoes no further decrease and reaches a constant value. This is the elutriation rate. The relationship observed by Wen and Chen between elutriation, entrainment, and bed height is

$$F = F_e + (F_o - F_e)\exp(-ah) \qquad (74)$$

F = entrainment rate, kg/m^{2}s
F_e = elutriation rate, kg/m^{2}s
F_o = entrainment rate at bed surface, kg/m^{2}s
h = height above bed surface, m
a = empirical constant, m^{-1}

The elutriation rate is determined from the following equations:

$$F_e = \quad F_{ei} \quad = \quad E_{ei}X_i \qquad (75)$$

$$E_{ei} = p_s(1 - e_i)u_{si} \qquad (76)$$

$$u_{si} = u_o - u_{ti} \qquad (77)$$

F_{ei} = elutriation rate for particle size i, kg/m^{2}s
E_{ei} = elutriation rate constant for particle size i, kg/m^{2}s
X_i = weight fraction in bed for particle size i
p_s = solid density, kg/m^3
e_i = fractional voidage in freeboard
u_{si} = solids velocity for particle size i, m/s
u_{ti} = terminal velocity for particle size i, m/s
u_o = superficial gas velocity, m/s

Voidage in the freeboard is calculated by

$$e_i = \left[1 + \frac{H(u_o - u_{ti})^2}{2gD_c}\right]^{-1/4.7} \qquad (78)$$

with H, the solids friction coefficient, obtained from the equations

$$\frac{Hp_s}{d_p^{\,2}}\left(\frac{v}{p_g}\right)^{2.5} = \begin{cases} 5.17Re_p^{-1.5}D_c^{\,2} & \text{for } Re_p < Re_{pc} \\ 12.3Re_p^{-2.5}D_c & \text{for } Re_p > Re_{pc} \end{cases} \qquad (79)$$

$$Re_p = p_g(u_o - u_{ti})d_p/v \qquad (80)$$

$$Re_{pc} = 2.38/D_c \qquad (81)$$

D_c = column diameter, m
g = acceleration of gravity, m/s^2
d_p = particle diameter, m
v = gas viscosity, kg/m-s
p_g = gas density, kg/m^3

The entrainment rate at the bed surface, F_o, is calculated as

$$\frac{F_o}{AD} = 3.07\times10^{-9}\frac{p_g^{3.5}g^{0.5}}{v^{2.5}}(u_o - u_{mf})^{2.5} \qquad (82)$$

A = column cross-sectional area, m^2
D = bubble diameter for bubbling bed,
  = column diameter for slugging bed, m
u_{mf} = minimum fluidization velocity, m/s

The particle terminal velocity is calculated from the equations suggested by Kunii and Levenspiel (1969):

$$u_t = \frac{g(p_s - p_g)d_p^2}{18v} \qquad Re \leqslant 0.4 \qquad (83)$$

$$u_t = d_p\left[\frac{4}{225}\,\frac{(p_s - p_g)^2g^2}{p_gv}\right]^{1/3} \qquad 0.4 < Re \leqslant 500 \qquad (84)$$

$$u_t = \left[\frac{3.1g(p_s - p_g)d_p}{p_g}\right]^{1/2} \qquad 500 < Re \leqslant 2\times10^5 \qquad (85)$$

$$Re = \text{Reynolds number} = d_pp_gu_t/v \qquad (86)$$

Jetting

Several investigators have developed correlations for jet penetration into a fluidized bed. Ghadiri and Clift (1980) compared several correlations and determined that all correlations except that of Merry (1975) grossly overpredicted the jet penetration. Merry's correlation for vertical jets in fluidized beds is

$$\frac{J}{d_o} = 5.2\left(\frac{p_g d_o}{p_s d_p}\right)^{0.3}\left[1.3\left(\frac{u_j^2}{g d_o}\right)^{0.2} - 1\right] \qquad (87)$$

where J = jet penetration height, m
d_o = jet nozzle diameter, m
u_j = jet nozzle velocity, m/s

Mass Transfer

In a model which includes multiple gas phases, mass transfer between the phases must be considered. Mass transfer of gaseous species between the emulsion and bubble phases can be calculated using the equation

$$r_i = K_{be,i} V_b (C_{e,i} - C_{b,i}) \qquad (88)$$

where r_i is the mass transfer rate of species i from the emulsion phase into the bubble phase, $K_{be,i}$ is the bubble-emulsion mass transfer coefficient for species i, V_b is the bubble volume, and $C_{e,i}$ and $C_{b,i}$ are the molar concentrations of species i in the emulsion and bubble phases. $K_{be,i}$ is given by

$$\frac{1}{K_{be,i}} = \frac{1}{K_{bc,i}} + \frac{1}{K_{ce,i}} \qquad (89)$$

$K_{bc,i}$ = bubble-cloud coefficient for species i
$K_{ce,i}$ = cloud-emulsion coeffiecient for species i

Kunii and Levenspiel (1969) have proposed correlations for the bubble-cloud and cloud-emulsion coefficients. The correlations are

$$K_{bc,i} = \frac{4.5u_{mf}}{d_b} + \frac{5.85D_{m,i}^{0.5}g^{0.25}}{d_b^{1.25}} \tag{90}$$

$$K_{ce,i} = 6.78\left(\frac{e_{mf}D_{m,i}u_b}{d_b^3}\right)^{0.5} \tag{91}$$

$D_{m,i}$ = diffusivity of component i in the gas mixture, ft^2/s
u_b = bubble velocity, ft/s
u_{mf} = min fluid velocity, ft/s
d_b = bubble diameter, ft
g = gravitational constant = 32.174 ft/s^2

In the gas inlet region, or grid region, of a gas fluidized bed, mass transfer occurs between the emulsion phase and the jet phase. Jet-emulsion mass transfer has not been studied to the same extent as bubble-emulsion mass transfer. Weimer (1978) estimated jet-emulsion mass transfer coefficients by multiplying bubble-emulsion coefficients by an empirical factor:

$$K_{je} = f_j K_{be}(v_b/v_j) \tag{92}$$

K_{je} = jet-emulsion mass transfer coefficient
K_{be} = bubble-emulsion mass transfer coefficient
v_b = bubble fraction
v_j = jet fraction
f_j = empirical factor

The factor f_j was varied from 5 to 90 in Weimer's study.

Behie and Kehoe (1973) developed a model to account for the effects of the grid region of fluidized-bed reactors. In their model the jet-emulsion mass transfer coefficients were estimated from the experimental data of Behie (1972). These data indicated that the factor f_j used by Weimer ranges from 40 to 60. The same approach to determining jet-emulsion mass transfer coefficients was used by Grace and de Lasa (1978).

A correlation to predict jet-emulsion coefficients was developed by Behie, et al.(1976). The correlation was based on data taken for CO_2 mass transfer in a fluidized bed of cracking catalyst. The correlation is

$$K_{je} = 0.48u_o\left(\frac{u_o^2}{gx}\right)^{-0.504}\left(\frac{d_o u_o p}{v}\right)^{0.068}\left(\frac{x}{d_o}\right)^{-0.095} \qquad (93)$$

K_{je} = jet-emulsion mass transfer coefficient, ft/s
u_o = jet velocity, ft/s
g = gravity constant, 32.174 ft/s^2
x = distance above jet inlet, ft
d_o = nozzle diameter, ft
p = gas density, lb/ft^3
v = gas viscosity, lb/(ft s)

Heat Transfer

Particle-gas heat transfer can be calculated using the following correlation presented by Kunii and Levenspiel (1969):

$$Nu_p = 0.3Re_p^{1.3} \qquad (94)$$

where Nu_p = particle Nusselt number = hd_p/k_g

Re_p = particle Reynolds number = $p_g d_p u_e/v_g$

h = heat transfer coefficient, Btu/(ft^{2}min^{o}R)
d_p = particle diameter, ft
k_g = gas thermal conductivity, Btu/(ft min^{o}R)
p_g = gas density, lb/ft^3
u_e = emulsion gas velocity, ft/s
v_g = gas viscosity, lb/(ft s)

The heat transfer rate is then given by

$$q = hS(T_s - T_e) \qquad (95)$$

q = heat transfer rate from particles to the emulsion gas, Btu/min
S = surface area of particles, ft^2
T_s = solids temperature, ^oR
T_e = emulsion phase temperature, ^oR

Kato and Wen (1970) studied solid-gas heat transfer in fluidized beds. The following equation was fit to Kato and Wen's data plot:

$$Nu = 0.316Pr^{1/3}Re^{1.1}(d/L_f)^{0.66} \qquad (96)$$

Pr = Prandtl number = $C_p v_g/k_g$
d = particle diameter, m
L_f = effective bed height for heat transfer, m

In the freeboard region of the reactor, heat transfer between the gas phase and coal particles can be estimated using single sphere heat transfer correlations. Eckert and Drake (1972) presented the following correlation

$$Nu = 2 + 0.236Re^{0.606}Pr^{1/3} \qquad (97)$$

and Kunii and Levenspiel (1969) proposed a similar relation

$$Nu = 2 + 0.6Re^{1/2}Pr^{1/3} \qquad (98)$$

Both are based on a single isolated spherical particle.

COAL GASIFICATION MODELING

Numerous models have been proposed to describe the gasification of char and coal. These models range from simple equilibrium-based models to complex kinetic models incorporating bed hydrodynamics and particle distributions.

Among the reactions commonly included in gasification models are the following:

$$C + H_2O = CO + H_2 \tag{99}$$

$$C + CO_2 = 2CO \tag{100}$$

$$C + 2H_2 = CH_4 \tag{101}$$

$$2C + H_2 + H_2O = CO + CH_4 \tag{102}$$

$$CO + H_2O = CO_2 + H_2 \tag{103}$$

$$C + 1/2\ O_2 = CO \tag{104}$$

$$C + O_2 = CO_2 \tag{105}$$

$$H_2 + 1/2\ O_2 = H_2O \tag{106}$$

$$CO + 1/2\ O_2 = CO_2 \tag{107}$$

$$CH_4 + 3/2\ O_2 = CO + 2H_2O \tag{108}$$

$$C + 2H_2O = CO_2 + 2H_2 \tag{109}$$

Reaction 99, the carbon-steam reaction, is the most important reaction in gasification, and along with reactions 101 and 103, the methanation and shift reactions, is included in nearly all gasification models. Reactions 104-108 are oxidation reactions which supply heat for the remaining reactions. Reactions 99, 101, and 102 are those by which Johnson (1974) of the Institute of Gas Technology (IGT) correlated gasification kinetic data. The kinetic rate expressions developed by Gibson and Euker (1975) and Feldman et al.(1972) are based on reactions 99 and 101. Both sets of reactions have often been used in gasification modeling.

FIXED-BED AND ENTRAINED-BED GASIFICATION MODELING

This research concerns only fluidized-bed gasification. However, fixed and entrained-bed models have much in common with fluidized-bed models. The same species and reactions are generally considered in each case, so that physical property data and reaction kinetics are similar. The differences are due to the different gas-solid contacting methods used in each reactor type.

Many fixed-bed models have been formulated, as the fixed-bed gasifier is the most fully developed commercial reactor type. Among the models are those by Stillman (1981), Joseph et al. (1981), Cho and Joseph (1981), Kosky and Floess (1980), Denn and Yu (1979), Biba et al. (1978), Amundson and Arri (1978), Yoon et al. (1978), and Winslow (1976).

Less work has been done on entrained-bed modeling, as until recently most developmental work was done with fixed and fluidized-bed reactors. More recently however, interest in entrained-bed reactors has increased, perhaps due to their lower production rates of tars and heavy hydrocarbons. Zahradnik (1973) has reviewed the chemistry and physics of entrained-bed gasification. Wen and Chaung (1979) formulated a model of the Texaco gasifier, and Sprouse (1980) has developed a model for the Rockwell International gasifier.

FLUIDIZED-BED GASIFICATION MODELING

A large number of studies have dealt with the modeling of fluidized bed gasifiers. The following paragraphs provide some details of selected fluidized-bed gasifier models.

The Institute of Gas Technology (1978) developed a model for char gasification based on the kinetics of Johnson (1974). The model assumes oxidation in a zone of negligible volume, followed by gasification in a perfectly-mixed zone. A set of design charts based on this model can be used to estimate reactor performance (IGT, 1978).

Pukanic et al.(1978) formulated a coal gasification model, based on Johnson kinetics for the gasification zone, with devolatilization products determined from stoichiometric considerations. The devolatilization and gasification zones are assumed to be well-mixed, as is the oxidation zone where all O_2 is consumed. The shift reaction is assumed to reach equilibrium.

Caram and Amundson (1979) examined the effects of bed hydrodynamics in fluidized-bed char gasification. Three models were studied: well-mixed solids and gases, the Kunii-Levenspiel (1969) fluidization model, and the fluidization model of Davidson and Harrison (1963). In addition, the kinetics of Johnson(1974) and the kinetics of Gibson and Euker(1975) and Feldman et al.(1972) were compared, as were the assumptions of agglomerating and nonagglomerating solids. The combustion zone was assumed to be of negligible volume with all O_2 consumption by reaction 105, and the shift reaction was assumed to proceed to equilibrium for all cases. Results indicated that the kinetics of Johnson provide good results over a wider range of pressure than Gibson-Euker-Feldman kinetics. The effect of agglomeration is small, while the bubble size is a very important factor.

Sundaresan and Amundson (1979a) developed models for char gasification which incorporated a distribution of particle conversions. The base model assumed a feed of uniform size and conversion, a well-mixed gasification zone, shift equilibrium, and formation of only CO_2 in a combustion zone of negligible volume. Johnson kinetics and Gibson-Euker-Feldman kinetics were both used. Comparison of results using the two sets of kinetics again indicated that Johnson kinetics provide a wider range of validity. Gibson-Euker-Feldman kinetics generally predict less methane, more hydrogen, and a lower gasification zone temperature than are predicted by Johnson kinetics. A second model based on the Davidson-Harrison two-phase fluidization model was then developed. Uniform sized bubbles, a perfectly-mixed emulsion phase, and isothermal operation were assumed. Comparisons with the single phase model revealed few differences in model predictions for small bubble diameters. However, for large bubbles, lower carbon conversion and reduced methane production are predicted by the two-phase model.

Sundaresan and Amundson (1979b) also studied the assumption of negligible oxidation zone volume. Well-mixed solids, plug flow of gases, and a shrinking core model for the carbon-oxygen reaction were assumed. The analysis indicated that the negligible oxidation zone volume assumption is generally good for most conditions encountered in fluidized-bed gasification.

Weimer (1978) developed a model for coal gasification which incorporated two-phase fluidization and a size distribution of solids. Devolatilization products were estimated from relations given by Field et al.(1967), and reactions 99, 100, 103-107, and 109 were assumed to occur in the fluidized bed. Simple first- and second-order rate equations were used. The model consists of a jetting region near the gas inlet, and emulsion and bubble phases above the jetting region. The general model was solved, along with a simplified case -- diffusion-controlled oxidation and reaction control of the C-H_2O and C-CO_2 reactions. In addition, cases with and without reaction in the jet and bubble regions were examined. Model results showed reasonably good agreement with published data. Consideration of reactions in the jet and bubble regions yielded decreased carbon conversions and decreased H_2/CO ratios compared to the case of no dilute phase reactions.

Weimer and Clough (1980) formulated a transient model which considered only equations involving the solid phase. Size and conversion distributions for the solids were considered, with the assumptions of constant density, only reactions 99, 100, 104, and 105 occurring, and uniform temperature throughout each particle. The model was used to examine the effects of upsets in the gas feed rate, solids feed rate, and size distribution of the solids feed on reactor behavior.

A slugging fluidized-bed model was developed by Wen and Tseng (1979). The model assumed three zones: a combustion zone where O_2 is present in both the bubble and emulsion phases, a gasification zone where O_2 is present only in the bubble phase, and a second gasification zone where no O_2 is present. In addition, devolatilization was considered, with the composition of the devolatilization gases based on the data of Loison and Chauvin (1964). Reactions 99-101, 103, 104, and 106-108 were assumed to occur in the fluidized bed. Plug flow of gases and well-mixed solids were also assumed. Model results compared well with experimental results from the Synthane process.

PILOT PLANT FACILITY

A complete description of the pilot plant facility is given by Ferrell et al., (1980). The plant consists of the following major subsystems: gasifier, raw gas cleaning, and acid gas removal. The following sections provide a description of each subsystem.

GASIFIER

The reactor, shown in Figure 8, is a 15.2 cm (6 in.) I.D. Schedule 40 pipe (316 SS) enclosed in several layers of Fiberfrax bulk ceramic insulation and contained in a 61 cm (24 in.) I.D. Schedule 80 carbon steel pipe. The overall height of the unit is roughly 3.7 m (12 ft). The gas feed is introduced into the reactor through three feed nozzles spaced triangularly near the bottom of the reaction chamber. Each nozzle consists of a 0.48 cm (3/16 in) orifice inside a diverging cone. Coal is fed at the top of the reactor and removed at the bottom by nitrogen-purged screw conveyors. The feed hopper is a 51 cm (20 in) I.D. schedule 80 carbon steel pipe, with a volume of 0.6 m^3 (22 ft^3). The char receiver is a 61 cm (24 in) I.D. Schedule 80 carbon steel pipe with a volume of 0.5 m^3 (18 ft^3).

The temperature profile in the bed is monitored by means of six thermocouples in a central thermowell in the reactor. The thermocouples are located at positions 13, 25, 64, 89, 114, and 140 cm (5,10,25,35,45,55 in) above the feed nozzles. The 25 cm thermocouple is used for reactor temperature control, with the oxygen feed rate being adjusted to maintain the selected temperature. A reactor pressure tap is located at the top of the reactor. Differential pressure taps on the gas feed line below the feed nozzles, at 38 cm and 89 cm above the feed nozzles, and at the top of the reactor are used to monitor the pressure drop across the feed cones and two pressure drops in the bed. The level of the fluidized bed is monitored with a nuclear level gauge, and is controlled by adjusting the char removal screw rotation rate. The height of the bed above the feed nozzles is normally 97 cm (38 in), although occasional runs with a 132 cm (52 in) bed have been made.

Nitrogen is supplied to the gasifier by a 23 m^3 (6000 gallon) liquid nitrogen tank and vaporizer system. Oxygen is fed from a manifold of six cylinders, and steam feed is from a 1135 kPa (150 psig) building process steam line.

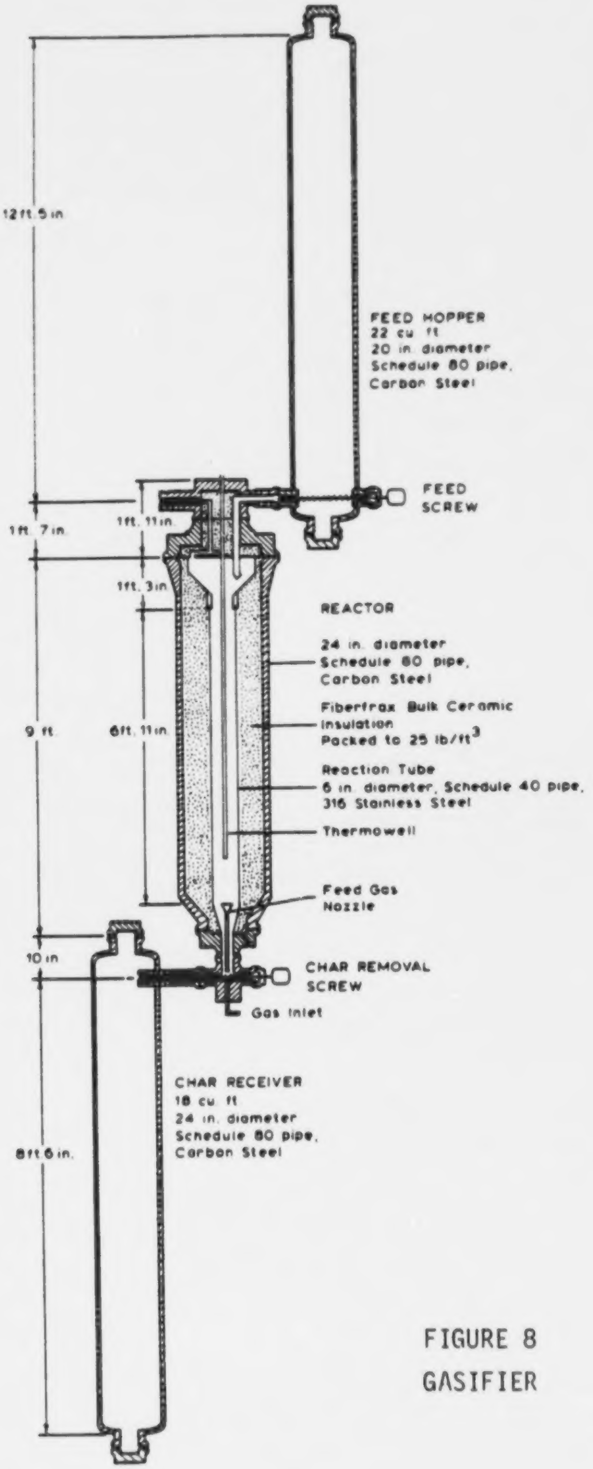
12 ft. 5 in.
FEED HOPPER
22 cu. ft
20 in. diameter
Schedule 80 pipe,
Carbon Steel
FEED
SCREW
1 ft. 7 in.
1 ft. 11 in.
1 ft. 3 in.
REACTOR
24 in. diameter
Schedule 80 pipe,
Carbon Steel
Fiberfrax Bulk Ceramic
Insulation
Packed to 25 lb/ft^3
Reaction Tube
6 in. diameter, Schedule 40 pipe,
316 Stainless Steel
Thermowell
9 ft.
6 ft. 11 in.
Feed Gas
Nozzle
10 in.
CHAR REMOVAL
SCREW
Gas Inlet
CHAR RECEIVER
18 cu. ft
24 in. diameter
Schedule 80 pipe,
Carbon Steel
8 ft. 6 in.

FIGURE 8
GASIFIER

PCS SYSTEM

The PCS (particulates, condensables, and solubles removal) system is shown in Figure 9. The gas exiting the gasifier is passed through a cyclone separator, where most of the elutriated particles are removed and collected in a fines collection vessel. After the cyclone, the gas line expands to 7.6 cm (3 in), and the gases pass through a scrubber system. The scrubber system consists of a set of three spray nozzles to quench the gas and a reduction of the pipe diameter to 2.5 cm (1 in) to promote gas-liquid contacting. The scrubber water is pumped by a 2.5 l/min (40 GPH) positive displacement pump, and may be either recirculated condensate or fresh city water.

The condensate accumulates in the PCS tank, a 2.5 m (8 ft) vessel with 0.9 m (3 ft) O.D. In the PCS tank a set of cooling coils -- three 6.1 m (20 ft) sections of 1.3 cm (1/2 in) tubing with city water as the coolant -- maintain the condensate temperature well below its boiling point. The emerging gas passes through a single-pass shell-and-tube heat exchanger, with city water on the shell side and the gases on the tube side. The exchanger is situated vertically above the PCS tank so that condensing water may run back into the tank. A demister, water separator, and coalescing filter are then used to remove any remaining water. The gas leaving the filter is either burned in a shielded flare or fed to the acid gas removal system.

Differential pressure taps measure the pressure drops across the cyclone, spray nozzles, and coalescing filter. The temperature is measured by thermocouples at five points in the PCS system. An orifice meter downstream of the filter is used to measure the make gas flow rate.

ACID GAS REMOVAL SYSTEM

The acid gas removal system (AGRS) is shown in Figure 10. Although not specifically a part of this research, the AGRS is a major portion of the pilot plant facility and thus will be described briefly. Kelly (1981) and Ferrell et al.(1980) provide detailed descriptions of the AGRS.

The major components of the AGRS are an absorption column, a flash tank, and a stripping column with the necessary auxiliary equipment. The major purpose of the system is to remove carbon dioxide and hydrogen sulfide from the gasifier make gas. In so doing it also usually removes most of the other sulfur gases and many of the hydrocarbons of molecular weight higher than methane. The system is modular in design so that alternative absorption processes can be evaluated. It was designed to

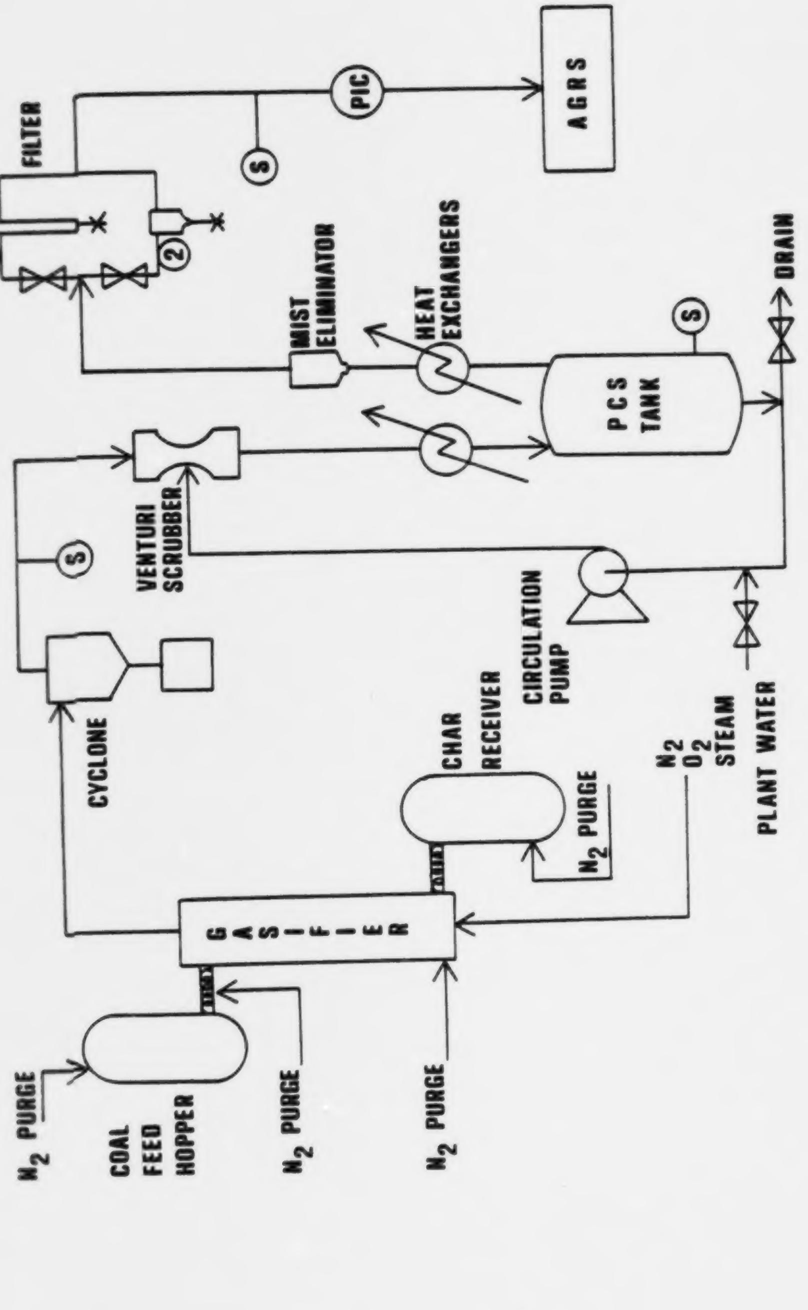
N_2 PURGE
COAL FEED HOPPER
N_2 PURGE
N_2 PURGE
GASIFIER
CHAR RECEIVER
N_2 PURGE
N_2
O_2
STEAM
PLANT WATER
CYCLONE
S
CIRCULATION PUMP
VENTURI SCRUBBER
PCS TANK
S
DRAIN
HEAT EXCHANGERS
MIST ELIMINATOR
①
②
FILTER
S
PIC
AGRS

FIGURE 9
PCS SYSTEM

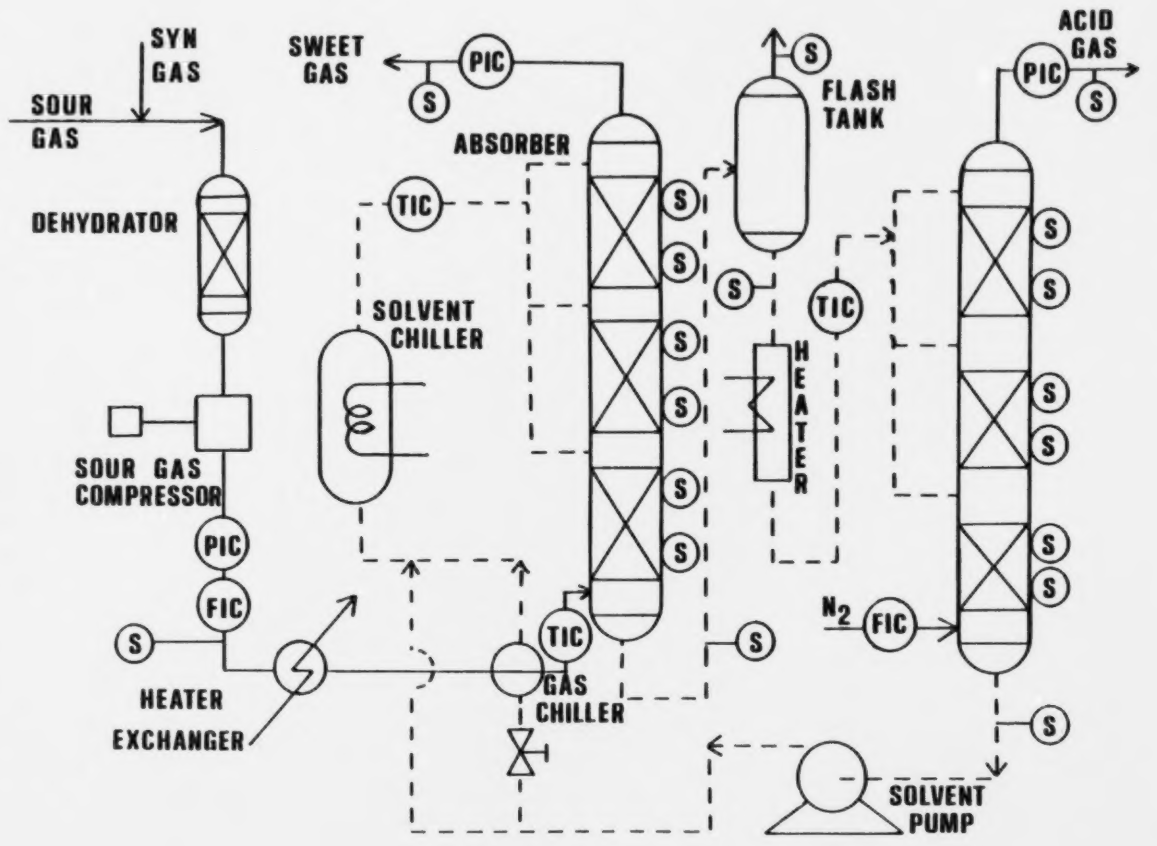
SYN GAS
SOUR GAS
DEHYDRATOR
SOUR GAS COMPRESSOR
PIC
FIC
S
HEATER EXCHANGER
SWEET GAS
PIC
S
TIC
SOLVENT CHILLER
ABSORBER
S
S
S
S
S
S
TIC
GAS CHILLER
S
S
FLASH TANK
S
HEATER
TIC
ACID GAS
PIC
S
S
S
S
S
S
S
N_2
FIC
S
SOLVENT PUMP

FIGURE 10

ACID GAS REMOVAL SYSTEM

operate with four different solvents; however, refrigerated methanol has been the only solvent used so far.

Gases from the PCS system are fed through a pair of dehydrating towers, compressed, cooled, and fed to the absorber. The absorption column contains three sections of ceramic Intalox saddle packing. The column is well-insulated, and approaches adiabatic operation. The solvent exiting the absorber is fed to a flash tank where some of the absorbed gases are released. The solvent then exchanges heat with the solvent exiting the stripper and is fed to the stripper. The stripper is similar to the absorber in design in that it contains three packed sections of ceramic Intalox saddles. The column approaches adiabatic operation, and the solvent can be regenerated either by stripping with an inert gas or with reboiled methanol vapors.

DATA ACQUISITION AND PROCESS CONTROL

Approximately 100 process sensors are used to obtain information during pilot plant operation. The plant is controlled with a Honeywell TDC-2000 process control computer which has a capability of regulating 16 process control loops throughout the pilot plant. Also, an alarm system incorporating all process sensors calls attention to process problems by sounding an audible alarm and lighting an alarm light on a process schematic above the control panel. The alarm system can also be set to cause plant shutdown automatically at pre-set alarm points.

The 100 process sensors (temperatures, pressures, differential pressures, flow rates, and levels) are monitored through a data acquisition system linked to a PDP 11/34 minicomputer. Each sensor is interpreted every five seconds for display on a video terminal. The information is averaged and stored every five minutes on magnetic disk for future data reduction. The capability of plotting information from each process sensor for the previous hour on a video or hard-copy terminal during the run also exists. Strip chart recorders are used for continuous monitoring of process temperatures and selected process variables.

Willis (1981) gives a detailed description of the process control and data acquisition system.

REACTOR MODELING

The primary function of the NCSU gasification reactor is to provide a reproducible synthesis gas for studies of the potential environmental impact of coal gasification processes. The development of correlative and predictive models of the gasifier was felt to be an indispensable adjunct to planning and implementing the overall experimental program.

The simplest model studied was a well-mixed reactor model for char gasification, which neglects entrainment, jetting, and evolution of sulfur and nitrogen species, and assumes shift equilibrium and isothermal operation. The most complex case was a two-phase bubbling bed model which includes entrainment and jetting effects, and includes kinetic expressions for the shift reaction and evolution of sulfur species. Models of intermediate complexity were also examined, and the degree to which each new level of complexity provides improved data correlation was determined.

WELL-MIXED GASIFIER MODEL

The first stage of the modeling studies was to formulate the simplest possible model which incorporates the principal gasification reactions and the gross physical characteristics of the reactor, and to determine the degree to which the gasifier performance could be correlated by this model. A well-mixed fluidized-bed model was used for this purpose. The model assumes instantaneous devolatilization and oxidation, followed by gasification in a perfectly mixed bed. The model takes as input the average reactor bed temperature and pressure; the bed dimensions; feed rates of coal, steam, oxygen, and nitrogen;solids holdup in the bed; and ultimate analysis of the feed coal, and calculates carbon conversion and make gas flow rate and composition.

Gasification Kinetics

As presently operated, the N.C. State gasifier operates with top feed of coal. Devolatilization is assumed to reach completion in the time that the coal falls from the feed screw to the fluidized bed. Methods of determining the devolatilization product yields are described in a subsequent section of this report.

In the fluidized-bed, the following reactions are presumed to take place:

$$C + H_2O = CO + H_2 \tag{110}$$

$$C + 2H_2 = CH_4 \tag{111}$$

$$2C + H_2 + H_2O = CO + CH_4 \tag{112}$$

$$CO + H_2O = CO_2 + H_2 \tag{113}$$

$$C + 1/2O_2 = CO \tag{114}$$

$$C + O_2 = CO_2 \tag{115}$$

$$S + H_2 = H_2S \tag{116}$$

$$H_2S + CO_2 = COS + H_2O \tag{117}$$

Reactions 114 and 115 are the oxidation steps required to supply heat for the remaining reactions. These two reactions are assumed to occur instantaneously in a zone of negligible volume separate from the gasification zone. All oxygen in the feed gas is taken to be consumed to form CO and CO_2, with the combustion product distribution being governed by the relation:

$$C + aO_2 = (2-2a)CO + (2a-1)CO_2 \tag{118}$$

where a, the combustion product distribution coefficient, is an adjustable model parameter. A value of a = 0.5 indicates that all CO is formed, while a = 1.0 indicates that only CO_2 is formed.

Reactions 110-112 are the reactions with which Johnson (1974) at the Institute of Gas Technology correlated gasification kinetics data. Reaction 110 is the conventional steam-carbon reaction. Reaction 112 is assumed to be an independent reaction, although it is attainable as a linear combination of 110 and 111. The reactivity coefficient, f_o, which is an adjustable parameter whose values depend on the particular char used, has values ranging from 0.3 for low-volatile bituminous coal char to about 10 for North Dakota lignite (Johnson, 1974). The Johnson kinetic expressions are given by equations (35) and (36) and Table 5.

Reaction 113 is the water gas shift reaction. A model option allows the assumption of shift reaction equilibrium or the use of kinetic rate equations. The rate expression (equation (41)) used is that given by Wen and Tseng (1979).

The rate of Reaction 116 is estimated by assuming that the sulfur conversion equals the carbon conversion, and that all converted sulfur forms hydrogen sulfide. The flow rate of COS is then determined by assuming equilibrium of Reaction 117.

The equilibrium constants for the water gas shift reaction and the Johnson gasification reactions were taken from Lowry (1963) and fit to the equation

$$\ln K = a_0 / T + a_1 \qquad (119)$$

by linear regression (Alexander, 1978), where T is the temperature in degrees Rankine. The equilibrium data of Kohl and Riesenfeld (1979) were fit to the same equation. The results are given in Table 9.

TABLE 9
REACTION EQUILIBRIUM CONSTANTS

Reaction	a_0	a_1
110	-29010.6	17.09
111	17744.4	-12.23
112	-11266.2	4.86
113	8395.2	-4.29
117	7881.6	-1.35

Reactor Simulation

The computational procedure for the well-mixed reactor model is outlined in Figure 11. The model first calculates the product yields from the devolatilization and combustion stages, and determines the feed rate and composition of the solid feed to the gasification stage. An iterative procedure is then used to determine the flows from the gasification stage.

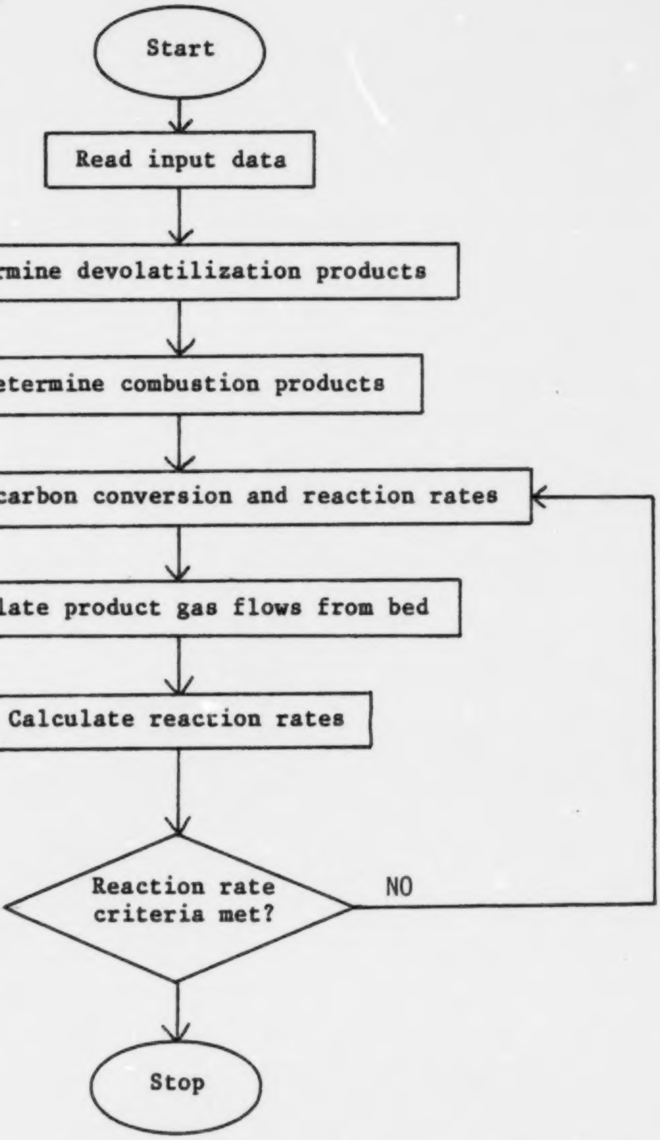
Start
Read input data
Determine devolatilization products
Determine combustion products
Estimate carbon conversion and reaction rates
Calculate product gas flows from bed
Calculate reaction rates
Reaction rate criteria met?
NO
Stop

FIGURE 11

WELL-MIXED MODEL COMPUTATIONAL PROCEDURE

In the devolatilization stage, the mass of coal devolatilized is determined, and the gas species flow rates are calculated. The devolatilized gases are then assumed to exit from the gasifier. The coal composition and flow rate are adjusted to reflect the loss of volatiles, and the resulting char constitutes the feed to the gasification stage.

In the combustion stage, the molar flow rates of carbon and oxygen are reduced from their feed values by amounts corresponding to complete consumption of oxygen, and the flow rates of CO and CO_2 are calculated as

$$q_{CO}' = [2(1-a)/a]q_{O2} \tag{120}$$

$$q_{CO2}' = [(2a-1)/a]q_{O2} \tag{121}$$

The effluent from the gasification stage is next estimated by assuming a carbon conversion of 20% in this stage (based on the carbon flow out of the devolatilization stage), with all conversion taking place by the steam-carbon reaction -- Reaction 110. The methane effluent rate is estimated to be 1% of the combined molar flow rates of CO, CO_2, H_2, and H_2O. The estimated effluent flow rates along with the reactor temperature and pressure determine the gas composition within the bed (ideal gas behavior is assumed). The component concentrations are then substituted into the kinetic equations to calculate the rates of Reactions 110-113.

The calculation of the correct effluent composition from the gasification stage is performed iteratively. In the first iteration, the rates of Reactions 110-113, $\{r_i^1\}$, calculated as described above, are compared to the following arbitrary values:

$$r_{110}^0 = 0.01 \tag{122}$$

$$r_{111}^0 = -0.0005 \tag{123}$$

$$r_{112}^0 = 0.0025 \tag{124}$$

$$r_{113}^0 = 0.002 \tag{125}$$

The first three rates are expressed as fraction of the base carbon consumed per minute, while the rate of Reaction 113 is in lb-moles/min. Convergence is said to be achieved if the percentage differences between successively determined rates are all less than 0.1%.

Following the calculation of $\{r_i^1\}$, new rates are calculated by modified successive substitution with convergence accelerated by the Dominant Eigenvalue Method (Orbach and Crowe, 1971). For each iteration, the dominant eigenvalue E of the vector of reaction rates is calculated:

$$E^k = \frac{\left\| r^{k-1} \right\|}{\left\| r^{k-2} \right\|} = \frac{\left[\sum (r_i^k - r_i^{k-1})^2 \right]^{0.5}}{\left[\sum (r_i^{k-1} - r_i^{k-2})^2 \right]^{0.5}} \qquad (126)$$

where the superscripts indicate the iteration number. Eigenvalue stability is considered to have been achieved when both of the following conditions are satisfied:

$$\left| (E^k - E^{k-1})/E^k \right| \leq 0.01 \qquad (127)$$

$$n \geq 5 \qquad (128)$$

where n is the number of iterations since eigenvalue stability was last achieved. When this condition is met, new rates are calculated as

$$r_i^{k+1} = r_i^{k-1} + p[(r_i^k - r_i^{k-1})/(1-E^k)]$$

where p is a damping factor.

When eigenvalue stability is not achieved (i.e., when equations (127) and (128) are not satisfied), new rates are calculated by modified successive substitution:

$$r_i^{k+1} = qr_{i,c}^k + (1-q)r_{i,e}^k \qquad (129)$$

where $r_{i,c}^k$ is a rate calculated in the k^{th} iteration from the kinetic rate equations, $r_{i,e}^k$ is an estimated rate for the k^{th} iteration, and q is a second damping factor. Preliminary studies showed that damping factor values p=0.7 and q=0.3 provide rapid and stable convergence; these values were therefore incorporated into the model program.

The new rates are used to calculate new product flow rates for the principal gas components:

$$q_{CO} = q_{CO}' + M_c(r_{110}+0.5r_{112}) - r_{113} \tag{130}$$

$$q_{CO2} = q_{CO2}' + r_{113} \tag{131}$$

$$q_{H2} = M_c(r_{110}-2r_{111}-0.5r_{112}) + r_{113} \tag{132}$$

$$q_{H2O} = q_{H2O}' + M_c(-r_{110}-0.5r_{112}) - r_{113} \tag{133}$$

$$q_{CH4} = M_c(r_{111}+0.5r_{112}) \tag{134}$$

where M_c is the base carbon feed to the fluidized bed and q_i' is the flow rate of component i leaving the first stage.

The newly determined product rates are then used in the kinetic rate expressions to calculate reaction rates, and convergence is again checked. This procedure is continued until the convergence criteria are satisfied. The reactor make gas composition and component flow rates are then determined by combining the gaseous effluents from the devolatilization and gasification stages.

TWO-PHASE GASIFIER MODEL

The two-phase bubbling-bed model of the NC State fluidized-bed gasifier divides the reactor into two main sections: a bed region, and a freeboard region above the bed. Consideration of a jetting region at the gas inlet of the bed is a model option that can add a third section to the model. The following paragraphs describe each section of the model and the overall structure of the program.

Freeboard Region

The NC State gasifier uses a top coal feeding system, with the feed particles falling through the hot exiting gas stream before entering the bed. In the freeboard region the particles are heated by the gas stream, and undergo drying and devolatilization. In addition, the fines in the coal feed stream may be eluted by the exiting gas stream. The model of the freeboard section accounts for all of these phenomena.

If elutriation is considered, the amount of fines blown out of the reactor is first calculated by assuming that all particles with terminal velocities less than the gas velocity at the top of the reactor are eluted. The blowover solids are assumed to undergo devolatilization at the gas exit temperature.

Following the blowover calculation, the flow rate and size distribution of the remaining coal are determined. The devolatilization products for this stream are calculated, assuming equilibrium yields at the temperature at the top of the bed. The devolatilization products are assumed to be evenly evolved along the length of the freeboard region. The details of these calculations are described in a later section of this report.

Heat transfer from the gas to the coal particles is calculated for each class of particle sizes using a single sphere heat transfer correlation given by Kunii and Levenspiel (1969). The correlation is given by equation (98). It is assumed that there are no radial temperature gradients within particles. The latent heat of devolatilization is neglected. The heat of vaporization of moisture is included in the model, with an average value of 37.7 kJ/gmol being used for all conditions. It is assumed that the heat required to vaporize the moisture in the feed coal is taken from the gas phase.

Particles are assumed to have constant volumes in the freeboard region, so that the particle densities decrease as drying and devolatilization proceed. No gas phase reactions are considered in this region.

Jet Region

The model contains an option to consider a jetting region at the gas inlet of the bed. The jet penetration height is first calculated using equation (87), which is a correlation of Merry (1975). This defines the thickness of the jet region. Merry also developed an expression for the jet angle, as indicated in Figure 12. The expression is

$$\tan(\quad) = 0.096 \left(\frac{p_s d_p}{p_g d_o} \right)^{0.3} \qquad (135)$$

where p_s and p_g are the solid and gas densities, and d_p and d_o are the particle and nozzle diameters. The jet diameter and the fraction of total bed cross section occupied by the jets at any height in the jet region can thus be calculated as

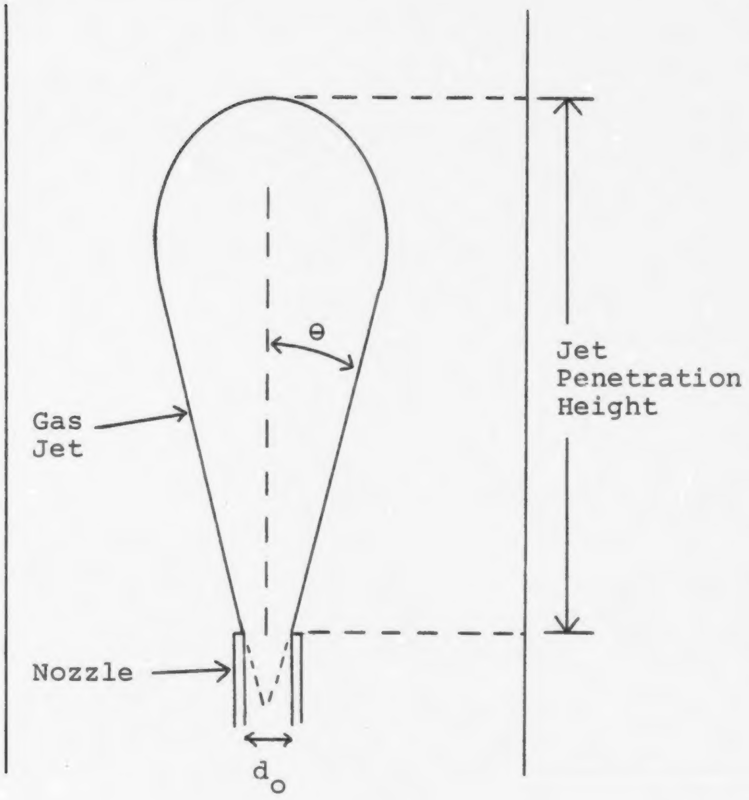
θ
Jet
Penetration
Height
Gas
Jet
Nozzle
d_o

FIGURE 12

GAS JET IN A FLUIDIZED-BED

$$d_j = 2h_j\tan(\quad) \tag{136}$$
$$v_j = n_j(d_j/d_c)^2 \tag{137}$$

where n_j is the number of gas nozzles, and d_j and d_c are the jet and column diameters. The remaining bed area is assumed to be at minimum fluidization conditions. The gases are assumed to be in plug flow, while the bed solids are assumed to be well-mixed with respect to composition and size. Mass transfer between the jet and emulsion phases is determined using the mass transfer coefficient correlation of Behie, et al.(1976). Equation (93) gives the Behie correlation.

Fluidized-Bed Region

The region between the jet penetration height and the top of the bed is assumed to be a two-phase fluidized region, consisting of an incipiently fluidized emulsion, and a solids-free bubble phase. Both gas phases are assumed to be in plug flow, while the solids are assumed to be perfectly mixed throughout the jet and fluidized-bed regions. The assumption of well-mixed solids throughout the the bed is supported by the experimental results. The minimum fluidization velocity (equation (59)) and the bed expansion ratio (equation (60)) are first calculated. The fraction of the bed occupied by bubbles is determined from the expansion ratio, and the emulsion gas and emulsion solids fractions are calculated from the emulsion phase voidage. The voidage is calculated from the following equation, which was fitted to data presented by the Institute of Gas Technology (1978).

$$e_{mf} = 0.449 + 145.0d_p \tag{138}$$

where d_p is the average particle diameter in ft. From the calculated flows and fractions, the average velocities of the bubble gas, the emulsion gas, and the solids are then determined.

Once the hydrodynamics of the fluidized region have been determined, reaction and mass transfer rates are calculated. Mass transfer between the two phases is calculated using mass transfer coefficients determined from the Kunii-Levenspiel correlations (1969). The bubble-emulsion mass transfer rates are calculated by using equations (88)-(91). In addition, transfer of gas may occur between phases when gas generation in the emulsion results in a flow rate greater than that needed for minimum fluidization. When this occurs, gas at the emulsion phase composition is transferred to the bubble phase until the emulsion phase gas flow is reduced to the minimum fluidization flow rate.

For both the jet and fluidized regions, the temperature may be determined in three manners:

- o specified isothermal temperature
- o imposed temperature profile
- o isothermal temperature calculated by model from energy balance

In all cases the solids and gases at any height are assumed to be at the same temperature.

Reaction Kinetics

The following reactions are assumed to occur in the emulsion phase:

$$C + H_2O = CO + H_2 \tag{139}$$

$$C + 2H_2 = CH_4 \tag{140}$$

$$2C + H_2 + H_2O = CH_4 + CO \tag{141}$$

$$C + O_2 = CO_2 \tag{142}$$

$$2C + O_2 = 2CO \tag{143}$$

$$S + H_2 = H_2S \tag{144}$$

$$CO + H_2O = CO_2 + H_2 \tag{145}$$

$$2CO + O_2 = 2CO_2 \tag{146}$$

$$2H_2 + O_2 = 2H_2O \tag{147}$$

$$CH4 + 2O_2 = CO_2 + 2H_2O \tag{148}$$

$$H_2S + CO_2 = COS + H_2O \tag{149}$$

The jet and bubble phases are solids-free, so that only reactions 145-147 may occur. Reactions 139-141 are the Johnson (1974) gasification reactions, with rates given by the previously discussed kinetic expressions (equations (35) and (36), and Table 5). The carbon combustion reactions, 142 and 143, are described by the rate equation of Parket and Hottel (1936). The combustion rate expression, given by equations (13)-(15), yields the rate of carbon consumption, but does not specify the gaseous products. The combustion product split between CO and CO_2 is therefore calculated from equation (18). The CO/CO_2 coefficient, a, can be determined from the correlation of Arthur (1951) (equation (19)), or left as an adjustable parameter.

Gas phase combustion occurs according to reactions 146-148. The reactions are very fast, and are assumed to go to instantaneous completion. In the event of insufficient oxygen for complete combustion, the reactions probably compete for oxygen at different rates. However, the reactions are expected to have a small overall effect on the model predictions, so for reasons of simplicity the three reactions are assumed to compete equally for the available oxygen.

The water gas shift reaction is considered to occur in both the bubble phase (jet phase in the jetting region) and emulsion phase. In the emulsion phase, the reaction occurs predominantly on the char surface, which acts as a catalyst. The rate equation used is that given by Wen and Tseng (1979). In the solids-free bubble phase, the rate expression is taken from Karim and Mohindra (1974). The rates of the shift reaction are given by equations (41) and (42). A model option also allows for the assumption of shift reaction equilibrium. The equilibrium constant is determined from equation (118) and the data of Table 9.

Hydrogen sulfide formation by reaction 144 can be calculated in two manners: use of the kinetic rate equations of Yergey et al.(1974) and Vestal et al.(1972), or by assuming equality of the sulfur and carbon conversions with all sulfur being converted to H_2S. The latter assumption is based on the experimental data given by Purdy (1983). The Yergey-Vestal kinetics are summarized by equations (43)-(52) and Table 7. The kinetic expressions are dependent on the sulfur form distribution. Based on the data of Purdy (1983) it is assumed that the sulfur form distribution following devolatilization consists of 1/3 FeS and 2/3 Organic III. Carbonyl sulfide is assumed to be formed only by reaction 149, which is assumed to be at equilibrium throughout the fluidized bed. Data for the sulfur shift reaction lends support to the assumption of equilibrium.

Computational Procedure

The overall computational procedure for the model is shown in Figure 13. Separate flowcharts of the iterative procedures for the bed and freeboard calculations are shown in Figures 14 and 15.

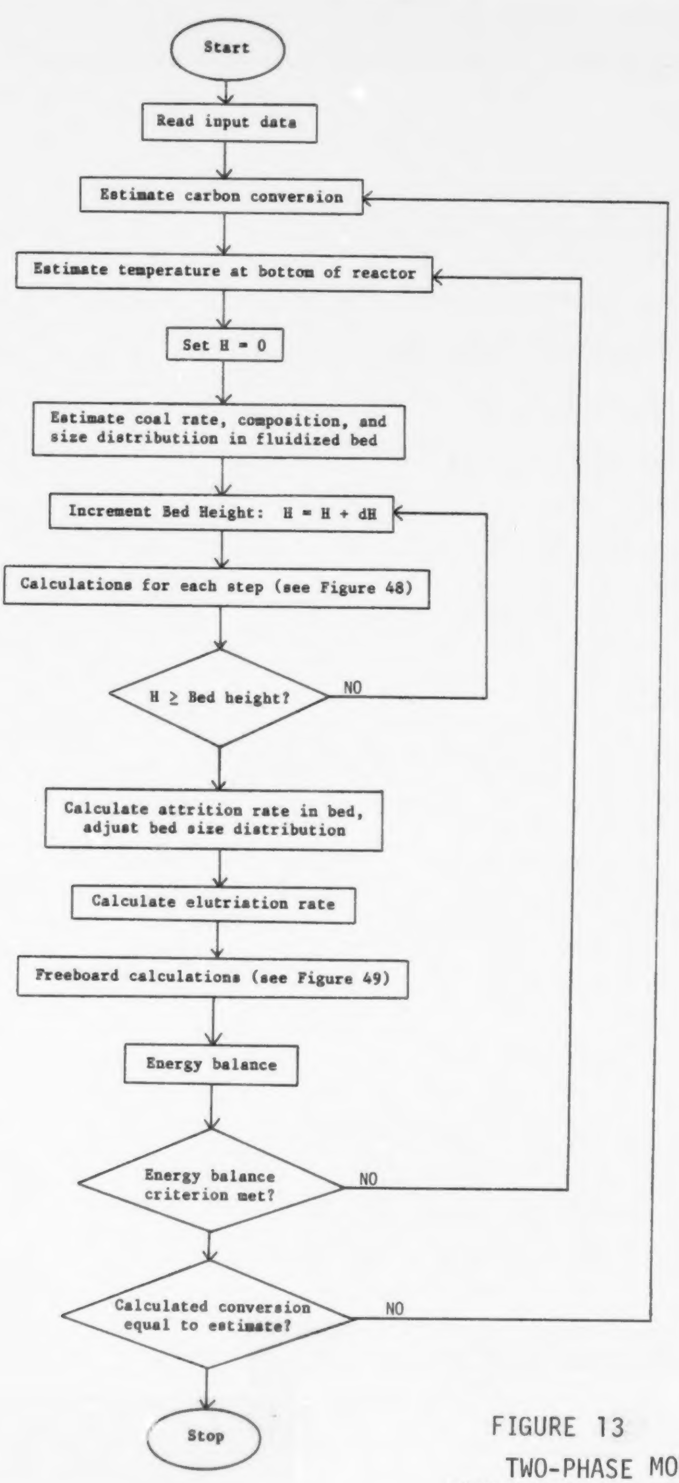
Start
Read input data
Estimate carbon conversion
Estimate temperature at bottom of reactor
Set H = 0
Estimate coal rate, composition, and size distributiion in fluidized bed
Increment Bed Height: H = H + dH
Calculations for each step (see Figure 48)
H ≥ Bed height?
NO
Calculate attrition rate in bed, adjust bed size distribution
Calculate elutriation rate
Freeboard calculations (see Figure 49)
Energy balance
Energy balance criterion met?
NO
Calculated conversion equal to estimate?
NO
Stop

FIGURE 13
TWO-PHASE MODEL
COMPUTATIONAL PROCEDURE

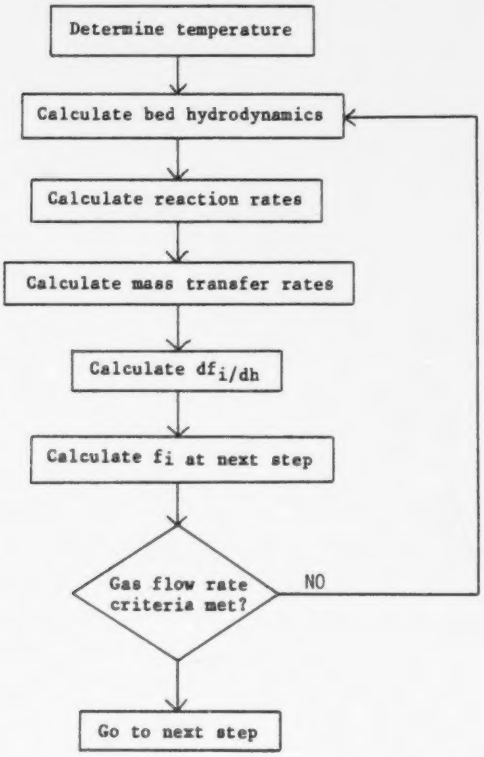
Determine temperature
Calculate bed hydrodynamics
Calculate reaction rates
Calculate mass transfer rates
Calculate $df_{i/dh}$
Calculate f_i at next step
Gas flow rate criteria met?
NO
Go to next step

FIGURE 14
COMPUTATIONAL PROCEDURE FOR BED CALCULATIONS

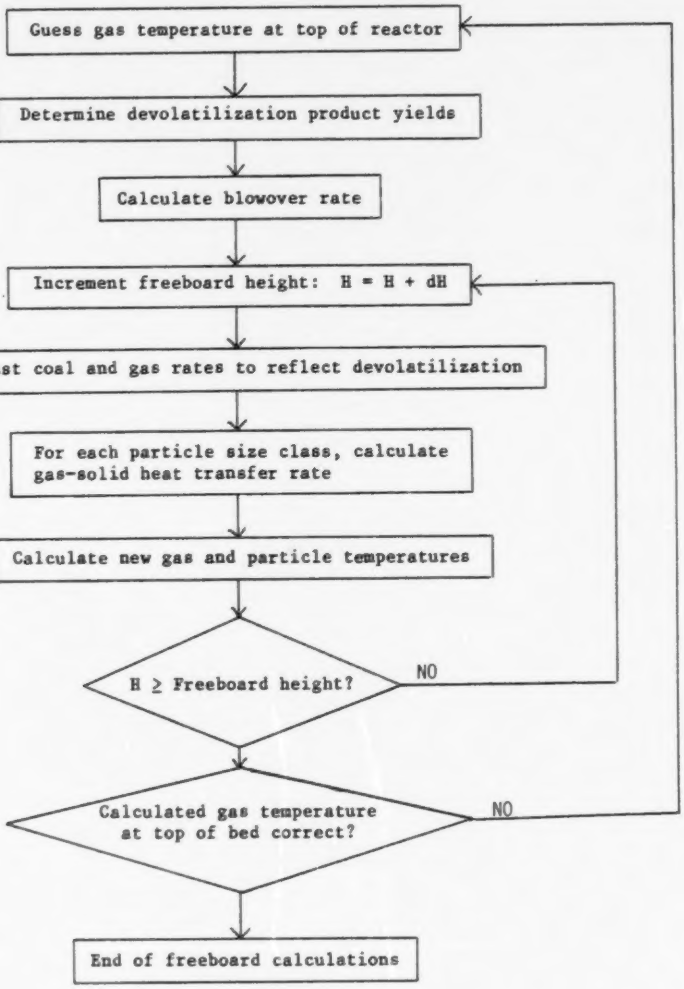
Guess gas temperature at top of reactor
Determine devolatilization product yields
Calculate blowover rate
Increment freeboard height: H = H + dH
Adjust coal and gas rates to reflect devolatilization
For each particle size class, calculate gas-solid heat transfer rate
Calculate new gas and particle temperatures
H ≥ Freeboard height?
NO
Calculated gas temperature at top of bed correct?
NO
End of freeboard calculations

FIGURE 15
COMPUTATIONAL PROCEDURE FOR FREEBOARD CALCULATIONS

The calculations are initiated by estimating the carbon conversion, composition, and temperature (if not specified) of the solids exiting the reactor. Stepwise calculations then proceed through both the jet and fluidized regions of the bed, starting at the bottom of the reactor where the gas feed conditions are known. At each step, the hydrodynamics (emulsion gas, bubble gas, and solids volume fractions, velocities, etc.) and the rates of reaction and mass transfer are calculated. The derivatives of species flows with respect to bed height are then calculated as

$$\frac{df_i}{dh} = \frac{\sum v_{i,k} r_k + N_i}{DH} \tag{150}$$

$v_{i,k}$ = stoichiometric coefficient for species i in reaction k
r_k = rate of reaction k
N_i = mass transfer rate between phases for species i
DH = step size used in calculations

A "predictor-corrector" method is used to determine the flow rates at the next point. Values are "predicted" by

$$f_{i,j+1} = f_{i,j} + (df_i/dh)_j (h_{j+1} - h_j)$$

$f_{i,j+1}$ = flow rate of species i at height j+1
$f_{i,j}$ = flow rate of species i at height j
$(df_i/dh)_j$ = derivative for species i evaluated at height j

From the predicted $f_{i,j+1}$, "corrected" values are calculated from

$$f_{i,j+1} = f_{i,j} + [(df_i/dh)_{j+1} + (df_i/dh)_j](h_{j+1} - h_j)/2 \tag{152}$$

where $(df_i/dh)_{j+1}$ is the derivative evaluated from the predicted $f_{i,j+1}$. The corrector equation is repeatedly applied until successive values agree within 1%.

For the first set of bed calculations, the solids size distribution in the bed is estimated and elutriation is neglected. Following the completion of bed calculations, size reduction and elutriation of the solid particles can be included. The calculations are based on the gas rate and composition at the top of the fluidized bed. It is assumed that the particle density following drying and devolatilization remains constant during combustion and gasification, and that particles of all size classes react at the same rate. The assumption of equal reaction rates for all particle sizes is supported by information presented by Levenspiel (1972).

For the conditions in the NCSU gasifier, Levenspiel indicates that the coal combustion rate is reaction-controlled rather than diffusion-controlled. The other reactions occurring in the gasifier are much slower than combustion, so that reaction control of all gas-solid reactions is a reasonable assumption. Particle diameters therefore are reduced as the gas-solid reactions occur. In addition, size reduction rates due to abrasion are calculated from the correlation of Merrick and Highley (1974). The resulting average particle diameter for each class of particles is calculated as

$$d_i = d_{i,o}(W_{ex}/W_{in})^{1/3} - r_a t_s \tag{153}$$

d_i = average diameter of particle class i following combustion/gasification
$d_{i,o}$ = average diameter of particle class i following drying/devolatilization
W_{ex} = solids mass flow rate at bed exit
W_{in} = solids mass flow rate at bed inlet
r_a = abrasion rate
t_s = average solids residence time

The calculations of the d_i are iterative, with convergence accelerated by Wegstein's method (Cerny, 1981).

The elutriation rate from the bed is determined following the size reduction calculations. The correlation used is that given by Merrick and Highley (1974). The size distributions of the elutriated solids and the bottoms exit solids are then calculated, and the solids elutriated from the bed are added to the solids blown out at the top of the reactor to form the total elutriate flow.

The calculations for the freeboard region are iterative. The coal feed temperature and gas temperature at the top of the bed are known; however, neither the coal temperature at the top of the bed nor the gas temperature at the reactor outlet are known. Calculations are started by assuming that the gas exit temperature equals the average of the coal inlet temperature and the gas temperature at the top of the bed. Stepwise calculations then start at the top of the freeboard region and proceed to the top of the fluidized-bed. If the calculated gas temperature at this point is within 1% of the correct gas temperature the convergence criterion is satisfied. If the criterion is not met, then a new gas exit temperature estimate is obtained using Wegstein's method, and the calculations are repeated. The procedure is continued until the convergence criterion is satisfied.

When the calculations for the bed and freeboard regions are both completed, an energy balance is performed around the reactor, and the carbon conversion is calculated. The following criteria are then checked:

$$\left| \frac{X_c - X_e}{X_c} \right| \leq 0.01 \tag{154}$$

$$\left| \frac{(H_{out} + H_{rxn}) - H_{in}}{H_{out}} \right| \leq 0.01 \tag{155}$$

where X_c and X_e are the calculated and estimated carbon conversions, and H_{out}, H_{in}, and H_{rxn} are the outlet and inlet enthalpies and heat of reaction. If either criterion is not satisfied, new conversion and temperature estimates are obtained by Wegstein's method for the exit solids, and the entire procedure is repeated. For the case of a specified isothermal bed temperature or a specified bed temperature profile, the energy balance and equation (155) are omitted.

DEVOLATILIZATION MODELING

Devolatilization must be accounted for by the reactor model when a raw coal feedstock is gasified. A large amount of research on devolatilization products and kinetics has been performed, as discussed previously. Unfortunately, the coals used in the NC State gasifier have not been well studied, and few data suitable for use in modeling are available.

In an effort to supply the desired devolatilization data base, separately conducted bench-scale pyrolysis measurements were performed by Gilman (1983). A batch fluidized-bed pyrolysis reactor was used. The pyrolysis reactor was heated to peak temperatures of 400-1000°C, with heating rates of approximately 1-6°C/s. Water and tar were condensed in a cold trap, and gases were collected in stainless-steel bombs for gas chromatographic analysis. Tar and residual char were subjected to proximate and ultimate analyses. Mass balances generally closed to within 90%, with the error largely due to untrapped water.

The New Mexico subbituminous coal used in gasification runs was used by Gilman in a series of pyrolysis runs. Production rates of emitted species, calculated as weight percents of the dry ash-free feed coal, were measured. The data for the major gaseous species (CO,CO2,H2,CH4,H2S,COS) and tar were correlated with peak temperature by regression analysis. For most of the species, quadratic equations yielded satisfactory correlations, and cubic equations were used for the remainder. The correlations are given in Table 10.

TABLE 10
NEW MEXICO COAL PYROLYSIS CORRELATIONS

$$X = a + bT + cT^2 + dT^3$$

X=wt % of daf coal, T=temperature, °C

	a	bx100	$cx10^5$	$dx10^8$
Tar	-10.9159	10.3100	-8.7627	0
H_2	15.0623	-6.5414	9.0404	-3.9000
CO	2.9936	-1.1385	1.5404	0
CO_2	1.6018	0.0552	0.3995	0
CH_4	-3.3132	1.0802	-0.4203	0
H_2S	-0.4255	0.1581	-0.1098	0
COS	0.0083	-0.00097	0.00123	0

The experimental work of Gilman used slow heating rates atypical of pilot plant conditions, so that the applicability of the pyrolysis correlations was questionable. For this reason, fast heating rate pyrolysis data were also examined for potential use in gasifier modeling studies.

Friedman, et al.(1968) performed fast pyrolysis studies with a Wyoming subbituminous coal similar to the New Mexico subbituminous coal used in this research. A comparison of the analyses of the two coals is given in Table 11.

TABLE 11
COMPARISON OF SUBBITUMINOUS COALS

	Wyoming Subbituminous Friedman et al.(1968)	New Mexico Subbituminous NCSU
Proximate		
Volatile Matter	42.7	47.4
Fixed Carbon	57.3	52.6
Ultimate		
Carbon	74.1	78.5
Hydrogen	5.7	5.4
Oxygen	17.9	13.1
Nitrogen	1.3	1.8
Sulfur	1.0	1.2

Friedman's pyrolysis studies used a 4-m entrained particle reactor, with helium as the carrier gas. Particle residence times ranged from 0.4 to 2.0 s, and heating rates ranged from 200-1000^{o}C/s. Tar and the major gaseous species were quantified. For the range of conditions most nearly approximating the devolatilization zone of the NCSU gasifier, the ratio of tar to total volatiles was 0.34. Analysis of the major gases gave the normalized gas composition listed in Table 12.

TABLE 12
PYROLYSIS GAS COMPOSITION OF FRIEDMAN

Species	Mole %
Hydrogen	27.9
Carbon Monoxide	19.4
Carbon Dioxide	15.5
Methane	37.2

It is necessary to determine the total devolatilization weight loss before the data of Friedman can be used. An empirical correlation of Kau (1980) was used for this purpose. The correlation, which yields the equilbrium dry ash-free weight loss as a function of peak temperature, is given by equation (4) and Table 2. Since Friedman did not analyze for sulfur gases, the data of Gilman were used to obtain estimates of the H_2S and COS concentrations in the pyrolysis gas. The values used were 2000 ppm H_2S and 140 ppm COS on a dry basis.

PHYSICAL, TRANSPORT, AND THERMODYNAMIC PROPERTIES

The physical, transport, and thermodynamic properties built into a model can have a large effect on the model's ability to provide reasonable predictions of the performance of a process. For this reason, a major effort was made to incorporate accurate property data and property prediction methods into the gasifier models. The data and methods are summarized in the following sections.

Viscosity

Polynomial equations empirically fit to experimental data as a function of temperature are used to calculate pure component viscosities. The equations were taken from Rohsenow and Hartnett (1973), except for that for hydrogen sulfide, which was obtained by fitting data given by Perry and Chilton (1973). Table 13 lists the coefficients. Mixture viscosities are calculated using the Wilke method suggested by Reid, et al. (1977), and the method of Dean and Stiel (Reid et al., 1977) is used to account for pressure effects.

TABLE 13
GAS VISCOSITY EQUATIONS

$$V = a + bT + cT^2 + dT^3 + eT^4 + fT^5$$

V: micropoise, T: ^oK

	a	$b\times10^1$	$c\times10^4$	$d\times10^7$	$e\times10^{11}$	$f\times10^{13}$
O_2	-9.24	9.42	-9.03	5.92	-1.45	0
CO	23.64	5.88	-2.73	0.66	0	0
H_2	2.11	4.77	-9.98	16.10	-128.02	3.82
CH_4	1.09	4.09	-1.38	0	0	0
CO_2	-5.44	5.94	-2.59	0.65	0	0
N_2	5.22	7.23	-5.81	3.22	-7.02	0
H_2S	11.63	4.10	0	0	0	0
H_2O	9.65	2.93	0.92	-0.42	0	0

Diffusivity

Binary gas mixture diffusivities are calculated by the method of Brokaw (1969). The assumptions of ideality and similar molecular weights are included in the method, although the polarities of gases are considered by inclusion of the dipole moment.

Diffusivities in a multicomponent system are determined by the method recommended by Bird, et al. (1960). The equation used is

$$\frac{1}{D_{mi}C} = \frac{\sum[(D_{ij}C)^{-1}(y_jN_i - y_iN_j)]}{N_i - y_i \sum N_j} \tag{156}$$

D_{mi} = diffusivity of component i in the mixture
D_{ij} = binary gas diffusivity
C = total molar density
y_i, y_j = mole fractions
N_i, N_j = molar fluxes

Heat Capacity

The heat capacities of coal and coal chars are calculated using the empirical correlation of Janka and Malhotra (1971). The correlation is

$$C_{pm} = 0.17 + 1.1\text{x}10^{-4}T + (3.2\text{x}10^{-3} + 3.05\text{x}10^{-6}T)V \qquad (157)$$

C_{pm} = mean heat capacity, Btu/(lb^{o}F)
T = temperature, ^{o}F
V = weight percent volatile matter on dry basis

The correlation gives the mean heat capacity from T_{ref}=70^{o}F to T for the dry coal. The effects of moisture must be accounted for separately.

Gas heat capacities are calculated from equations given by Reid et al. (1977). The equations are given in Table 14. Gas mixture heat capacities are calculated as molar-weighted averages of the pure component heat capacities.

TABLE 14
GAS HEAT CAPACITY EQUATIONS

$C_p = a + bT + cT^2 + dT^3$

C_p: Btu/(lbmole^{o}R), T: ^{o}R

Species	a	bx10^3	cx10^6	dx10^{10}
O_2	6.713	-4.88x10^{-4}	1.287	-4.362
CO	7.373	-1.706	2.056	-5.207
H_2	6.483	1.231	-1.018	3.131
CH_4	4.598	6.917	0.882	-4.635
CO_2	4.728	9.744	-4.129	7.025
N_2	7.440	-1.80	1.975	-4.784
H_2S	7.629	0.1906	1.793	-4.818
COS	5.629	10.59	-5.172	10.05
H_2O	7.701	0.2553	0.778	-1.473

Thermal Conductivity

Pure component gas thermal conductivities as a function of temperature are calculated by fitting equations suggested by Rohsenow and Hartnett (1973) to data tabulated by Weast (1970) and Rohsenow and Hartnett (1973). Mixture thermal conductivities are calculated by the method suggested by Perry and Chilton (1973), with a pressure correction by the method of Stiel and Thodos (1964).

Heats of Formation and Reaction

Heats of reaction were calculated using heat of formation data given by Felder and Rousseau(1978). All values are at 25°C, and presume gaseous products. Tables 15 and 16 list the heats of formation and the calculated heats of reaction.

TABLE 15
HEATS OF FORMATION

Species	Heat of Formation, kJ/mol
O_2	0.0
CO	-110.52
H_2	0.0
CH_4	-74.85
CO_2	-393.5
N_2	0.0
H_2S	-19.96
COS	-138.4
H_2O	-241.8

TABLE 16
HEATS OF REACTION

Reaction	Heat of Reaction kJ/mol
$C + H_2O = CO + H_2$	1.31×10^{-2}
$C + 2H_2 = CH_4$	-7.48×10^{-3}
$C + 0.5H_2 + 0.5H_2O = 0.5CH_4 + 0.5CO$	2.83×10^{-3}
$C + CO_2 = 2CO$	1.72×10^{-2}
$CO + H_2O = CO_2 + H_2$	-4.11×10^{-3}
$C + 0.5O_2 = CO$	-1.10×10^{-2}
$C + O_2 = CO_2$	-3.92×10^{-2}
$2CO + O_2 = 2CO_2$	-5.64×10^{-2}
$2H_2 + O_2 = 2H_2O$	-4.83×10^{-2}
$0.5CH_4 + O_2 = 0.5CO_2 + H_2O$	-4.02×10^{-2}
$S + H_2 = H_2S$	2.01×10^{-3}
$FeS_2 + H_2 = FeS + H_2S$	1.03×10^{-2}
$FeS + H_2S = Fe + H_2S$	1.15×10^{-2}

Critical Data

Critical constants are required for the calculation of diffusivity, and the calculation of mixture viscosity and thermal conductivity. Table 17 gives the critical temperatures, volumes, and compressibility factors for the species considered in this work. The data were taken from Reid, et al.(1977).

TABLE 17
CRITICAL CONSTANTS

Species	T_c, K	V_c, $cm^3/gmol$	Z_c
O_2	154.6	73.4	0.288
CO	132.9	93.1	0.295
H_2	33.2	65.0	0.305
CH_4	190.6	99.0	0.288
CO_2	304.2	94.0	0.274
N_2	126.2	89.5	0.290
H_2S	373.2	98.5	0.284
COS	375.0	140.0	0.260
H_2O	647.3	56.0	0.229

MODELING RESULTS

WELL-MIXED MODEL

In its present form, the model has three adjustable parameters:

1. The coal reactivity coefficient, f_o.
2. The combustion product distribution coefficient, a, which specifies the split between CO and CO_2 in the products of the combustion stage of the gasification.
3. The water gas shift reactivity parameter, f_{wg} .

These parameters were evaluated by using a Pattern Search routine (Beightler et al.,1979) to minimize a function of the sum of squared deviations between predicted and measured values of gasifier performance variables. The function is

$$Y = \frac{1}{n}\sum\left\{ \left(\frac{F_p - F_m}{F_m}\right)^2 + \left(\frac{f_p - f_m}{f_m}\right)^2 + \frac{1}{3}\left[\left(\frac{y_{H2,p} - y_{H2,m}}{y_{H2,m}}\right)^2 + \left(\frac{y_{CO,p} - y_{CO,m}}{y_{CO,m}}\right)^2 + \left(\frac{y_{CO2,p} - y_{CO2,m}}{y_{CO2,m}}\right)^2\right]\right\} \qquad (158)$$

where F is the dry make gas flow rate, f is the total carbon conversion, y_i is the mole fraction of gas i in the product gas, n is the number of experimental runs in the data base, and the subscripts p and m indicate predicted and measured values. The runs with the best mass balance closures were chosen to provide the data base for the parameter estimation.

Kentucky Bituminous Char

The set of runs chosen to provide the data base for parameter estimation was a subset of those available for the Kentucky bituminous char. Using this data base, the objective function Y of equation (158) was minimized to yield the following parameter values:

$$f_o = 0.276 \qquad (159)$$

$$a = 0.828 \qquad (160)$$

$$f_{wg} = 1.29\times10^{-5} \qquad (161)$$

Substitution of the value of a given above into equation (18) indicates that 66% of the carbon oxidized forms CO_2 and 34% forms CO. An equation by Arthur (1951) predicts a = 0.57 at 1400°F and a = 0.52 at 2000°F, while several gasification studies have assumed a = 1.0 (Caram et al.,1979; Institute of Gas Technology,1978; Pukanic et al.,1978; Sundaresan and Amundson,1979).

The value of $f_{wg} = 1.29\times10^{-5}$ indicates that the shift reaction rate is approximately five orders of magnitude less than the rate typically obtained in catalytic shift reactors. Wen and Tseng (1979) used a shift reactivity value of 1.7×10^{-4} in modeling the gasification of a bituminous coal by the Synthane process. The larger value used by Wen and Tseng may be attributed to the differences in the coals used in both studies.

Using the optimal parameter values, the model was run for all char runs. Plots of predicted vs measured values of carbon conversion, dry make gas flow rate, and sweet gas heating value are shown in Figures 16-18. (The sweet gas is defined as the dry make gas with the CO_2 and H_2S removed.) The close proximity of the points to the 45 degree line is gratifying in view of the simplicity of the model.

The model also does a creditable job of correlating data on the evolution of individual species. Figures 19-22 show predicted versus measured production rates of hydrogen, carbon monoxide, carbon dioxide, and water. The correspondence between prediction and measurement suggests that the model can be used to predict the composition of the gasifier make gas for a specified set of reactor conditions, and also to study the effects of individual reactor variables on product yields.

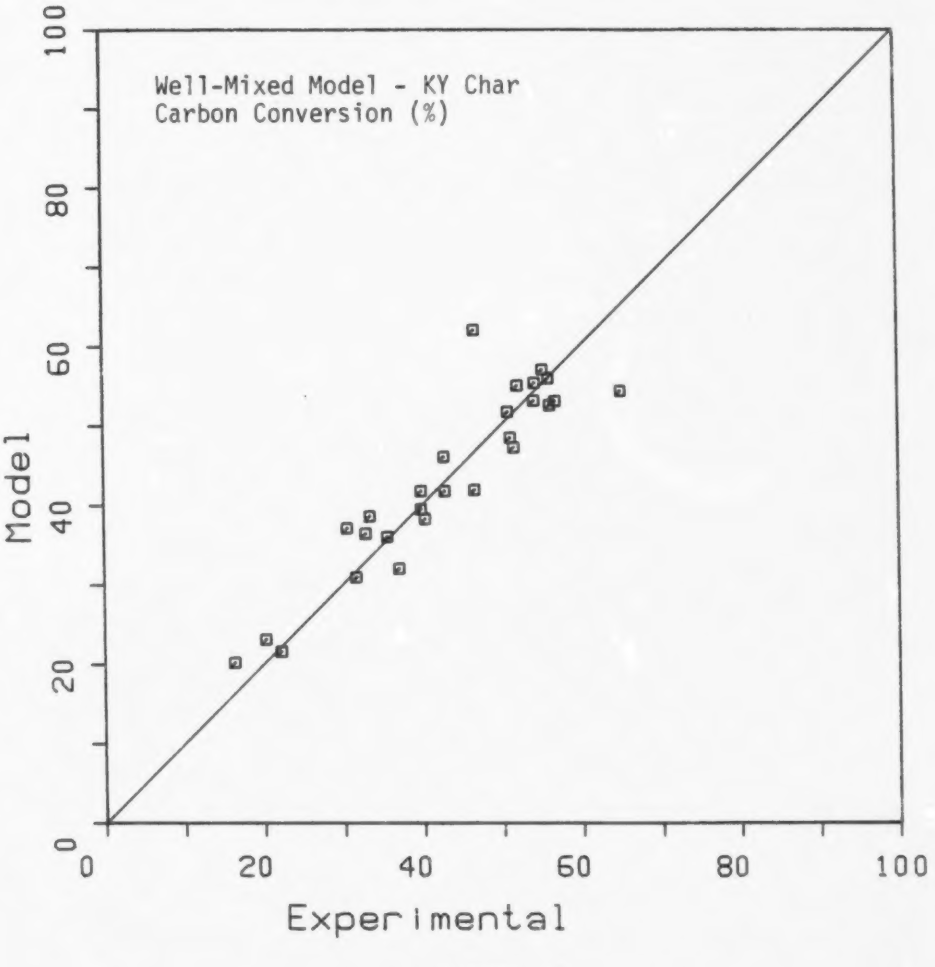

FIGURE 16

PREDICTED VS. EXPERIMENTAL CARBON CONVERSION
FOR KY CHAR, WELL-MIXED MODEL

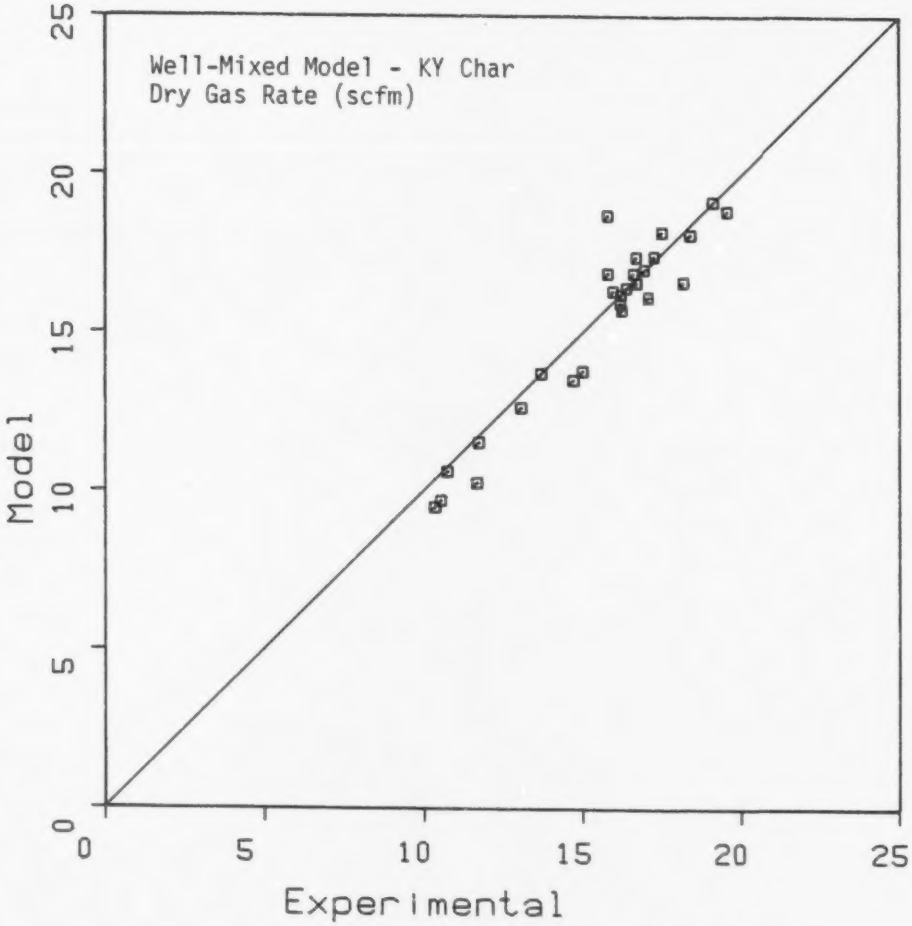

FIGURE 17

PREDICTED VS. EXPERIMENTAL GAS PRODUCTION RATE
FOR KY CHAR, WELL-MIXED MODEL

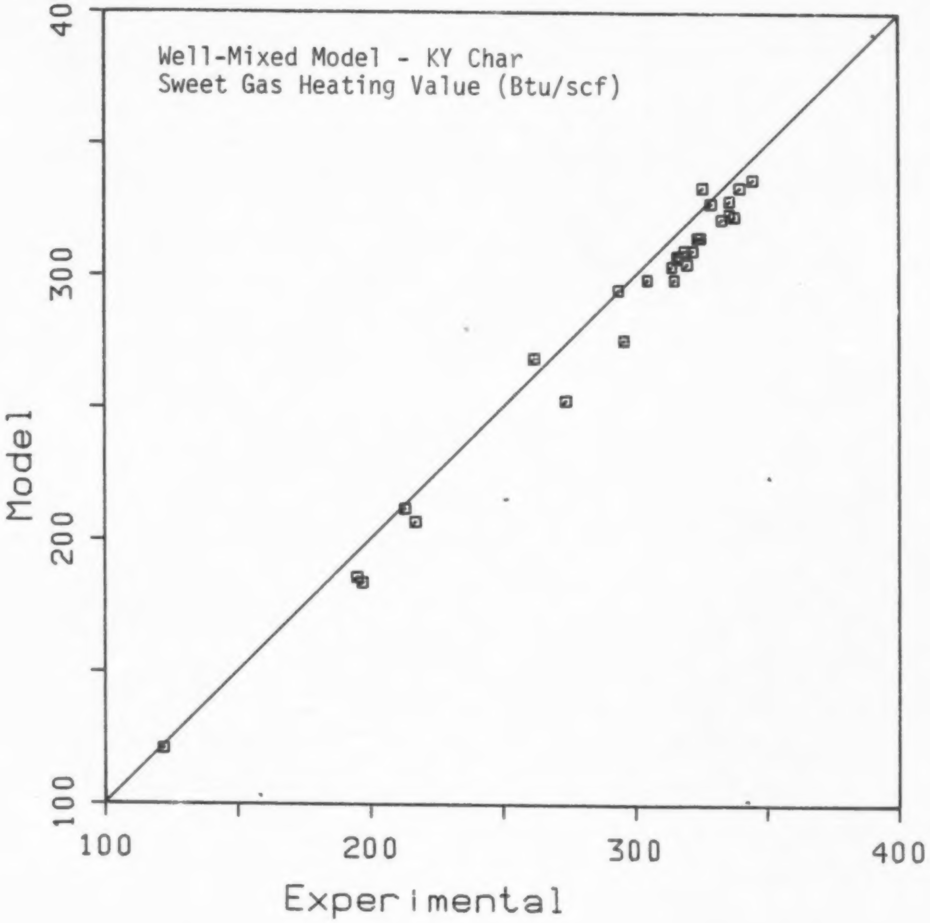

FIGURE 18

PREDICTED VS. EXPERIMENTAL HEATING VALUE
FOR KY CHAR, WELL-MIXED MODEL

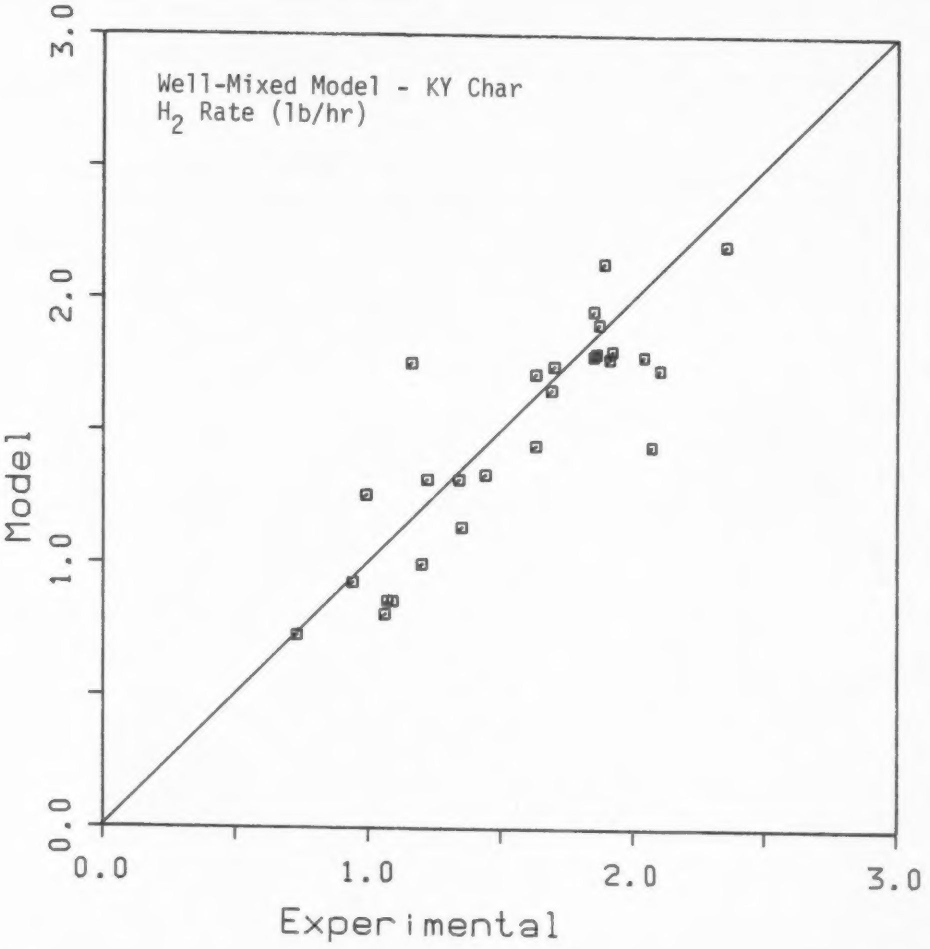

FIGURE 19

PREDICTED VS. EXPERIMENTAL HYDROGEN PRODUCTION RATE
FOR KY CHAR, WELL-MIXED MODEL

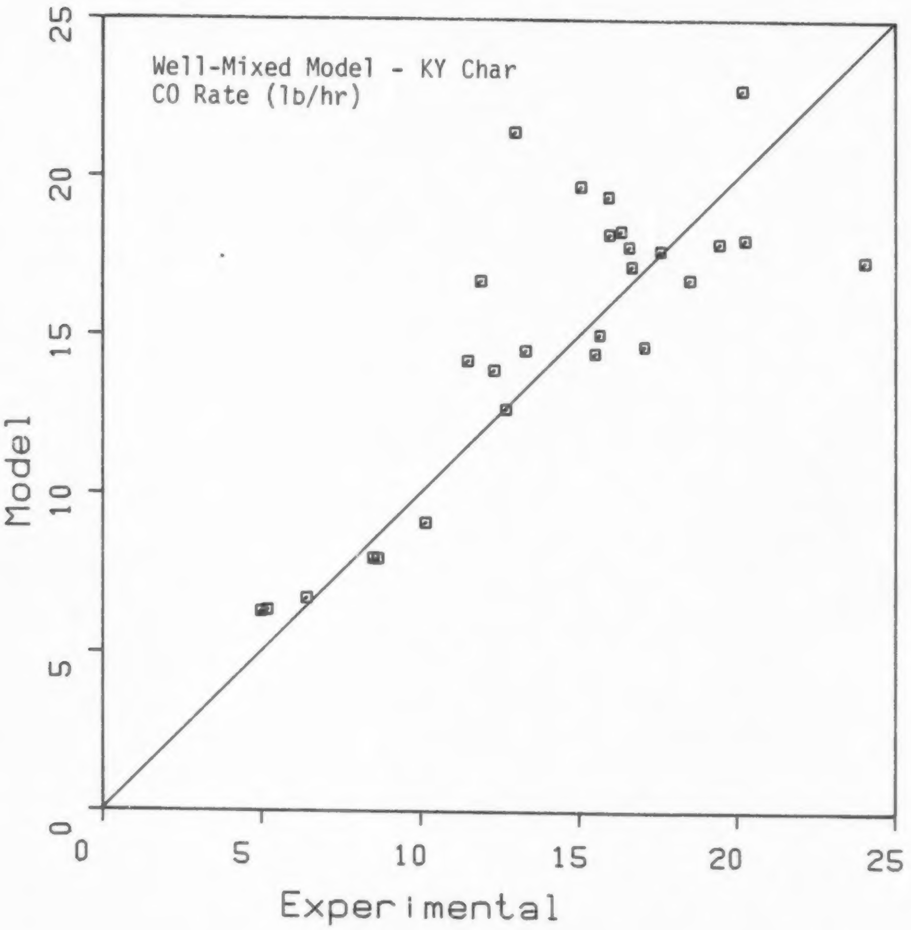

FIGURE 20

PREDICTED VS. EXPERIMENTAL CARBON MONOXIDE PRODUCTION RATE FOR KY CHAR, WELL-MIXED MODEL

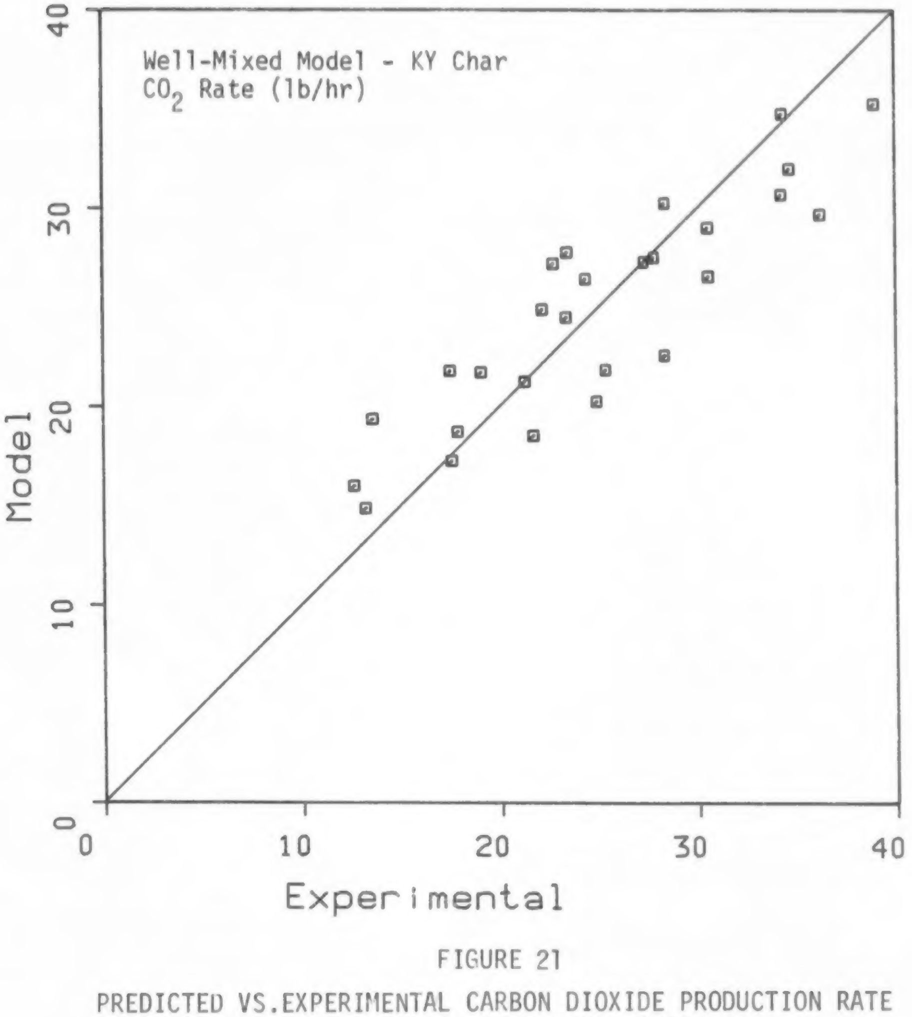

FIGURE 21

PREDICTED VS.EXPERIMENTAL CARBON DIOXIDE PRODUCTION RATE FOR KY CHAR, WELL-MIXED MODEL

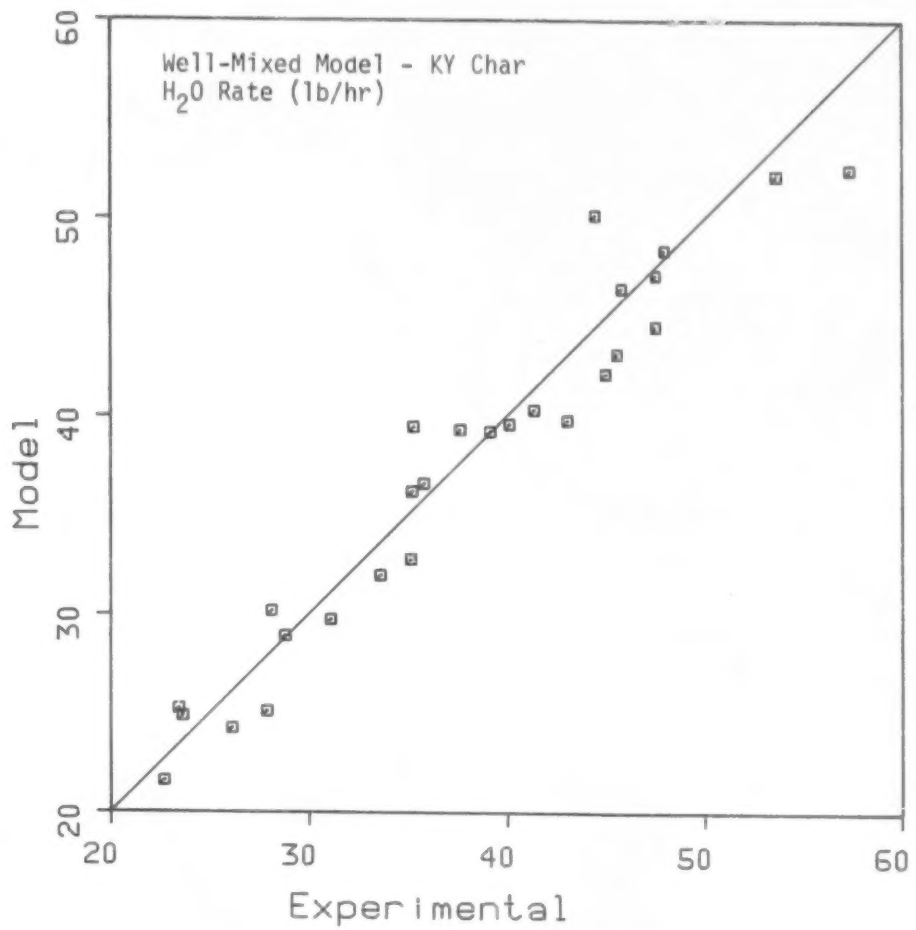

FIGURE 22

PREDICTED VS. EXPERIMENTAL WATER EVOLUTION RATE
FOR KY CHAR, WELL-MIXED MODEL

New Mexico Subbituminous Coal

The same optimization procedure used to determine the optimal parameters for char was employed to find the optimal parameter values for the New Mexico subbituminous coal. The initial efforts were made with the devolatilization product correlations of Gilman (1983) incorporated into the model. Use of the optimal parameter values yielded results that were unsatisfactory. Predictions of the major reactor performance variables, such as the gas production rate and carbon conversion, agreed reasonably well with experimental results. However, correlations of the individual gas production rates were not acceptable. The reason for the poor species correlations was probably the use of slow pyrolysis data to describe the devolatilization zone of the reactor.

In an effort to improve the correlations obtained from the model, the fast pyrolysis product data of Friedman, et al.(1968) were used to calculate the devolatilization gas product distributions. Using this model, equation (158) was again minimized to determine the optimal parameter values. The resulting values were:

$$f_0 = 4.20 \tag{162}$$

$$a = 1.00 \tag{163}$$

$$f_{wg} = 1.2\text{x}10^{-4} \tag{164}$$

The char reactivity parameter for coal is much larger than that obtained for the Kentucky char. The combustion coefficient does not differ greatly for the coal and the char; however, the shift reactivity parameter is an order of magnitude greater for the coal than for the char. A possible reason for the greater shift reactivity of the New Mexico coal compared to the char is the different ash contents of the two materials: the coal had an feed ash content of 22.6%, while the ash content of the char was only 10.7%. The minerals in the ash fraction of coal serve as catalysts for the shift reaction. In addition, during gasification the coal was converted to a greater extent than the char, giving an even larger difference in ash contents. The shift reactivity parameter obtained in this study for a subbituminous coal agrees well with the value used by Wen and Tseng (1979) for a bituminous coal (f_{wg} = $1.7\text{x}10^{-4}$).

The model was used to correlate the New Mexico coal run data using the optimal parameter values. In general, the agreements between model predictions and experimental measurements were excellent. Comparisons of predicted and measured reactor variables are shown in Figures 23-31. Figures 23 and 24 are correlation plots for carbon conversion and the dry make gas flow rate. Plots for individual gas species production rates are shown in Figures 25-31 for CO, CO_2, H_2, CH_4, H_2O, H_2S, and

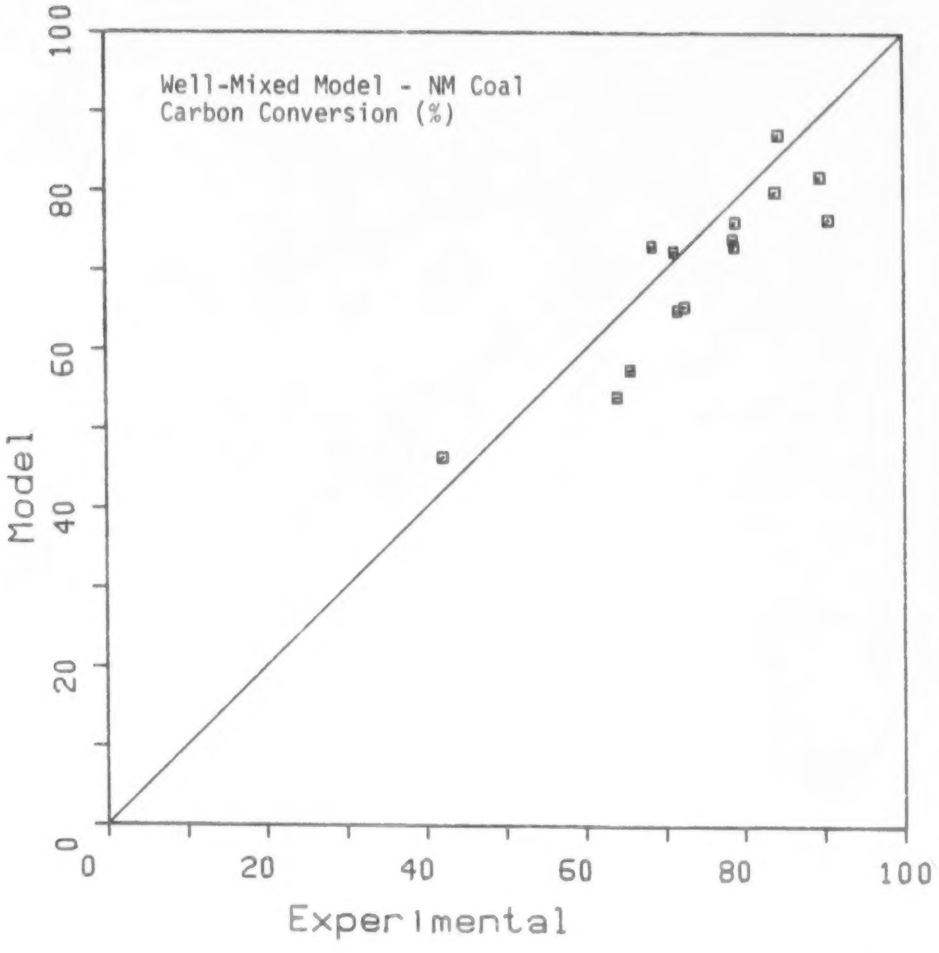

FIGURE 23

PREDICTED VS. EXPERIMENTAL CARBON CONVERSION
FOR NM COAL, WELL-MIXED MODEL

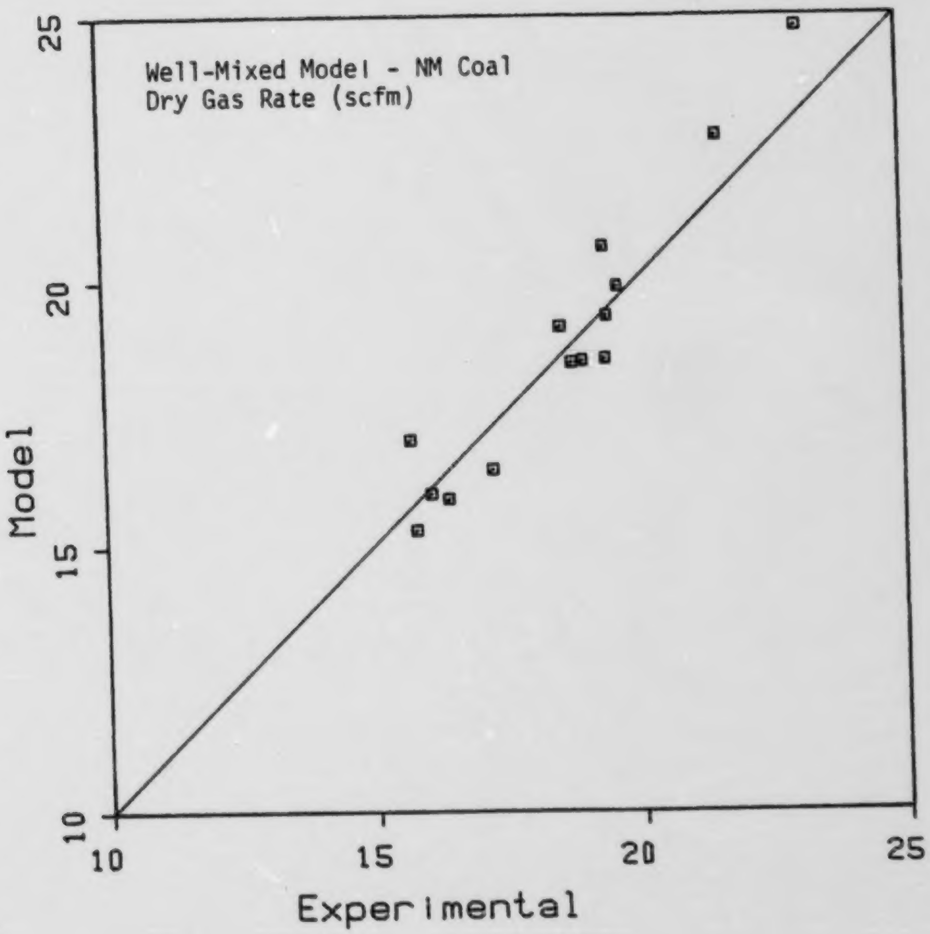

FIGURE 24

PREDICTED VS. EXPERIMENTAL GAS PRODUCTION RATE FOR NM COAL, WELL-MIXED MODEL

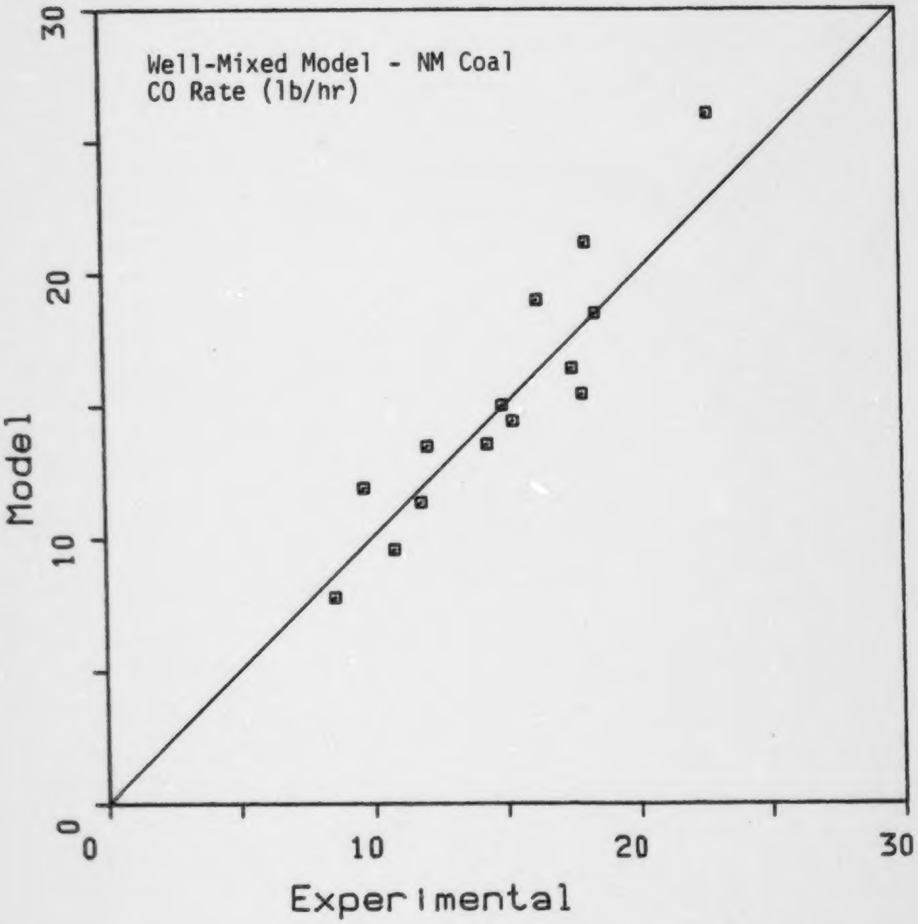

FIGURE 25

PREDICTED VS. EXPERIMENTAL CARBON MONOXIDE PRODUCTION RATE FOR NM COAL, WELL-MIXED MODEL

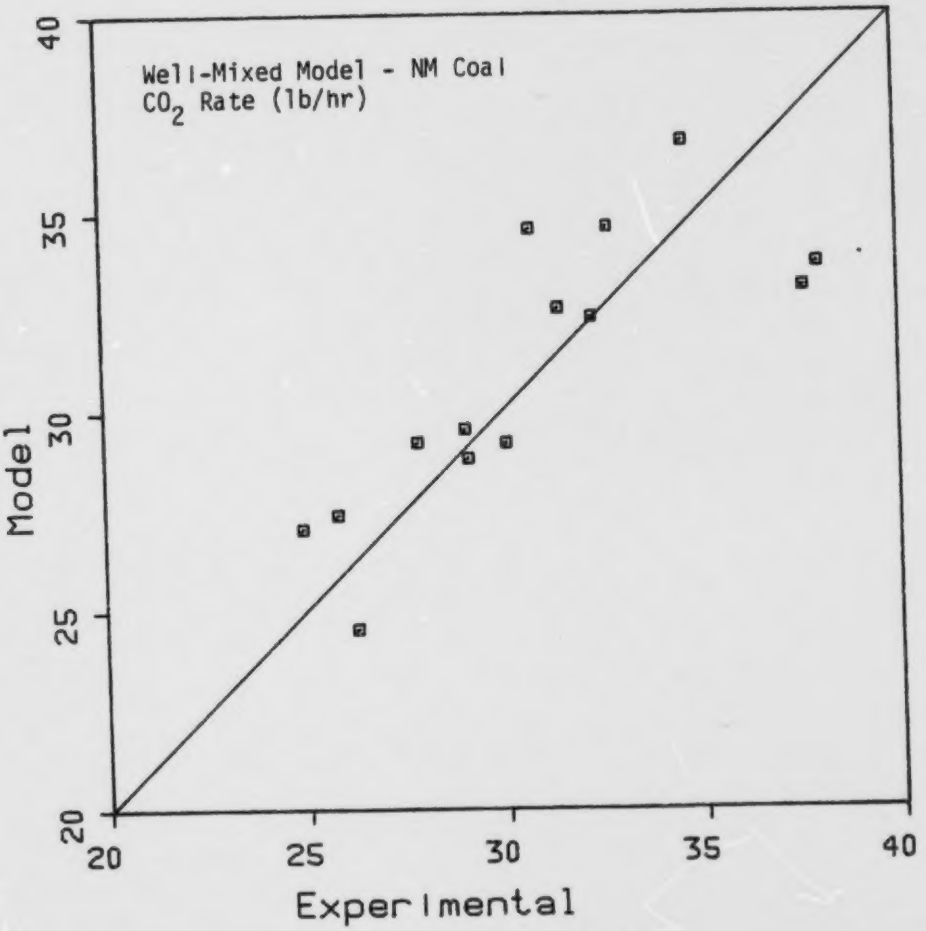

FIGURE 26

PREDICTED VS. EXPERIMENTAL CARBON DIOXIDE PRODUCTION RATE FOR NM COAL, WELL-MIXED MODEL

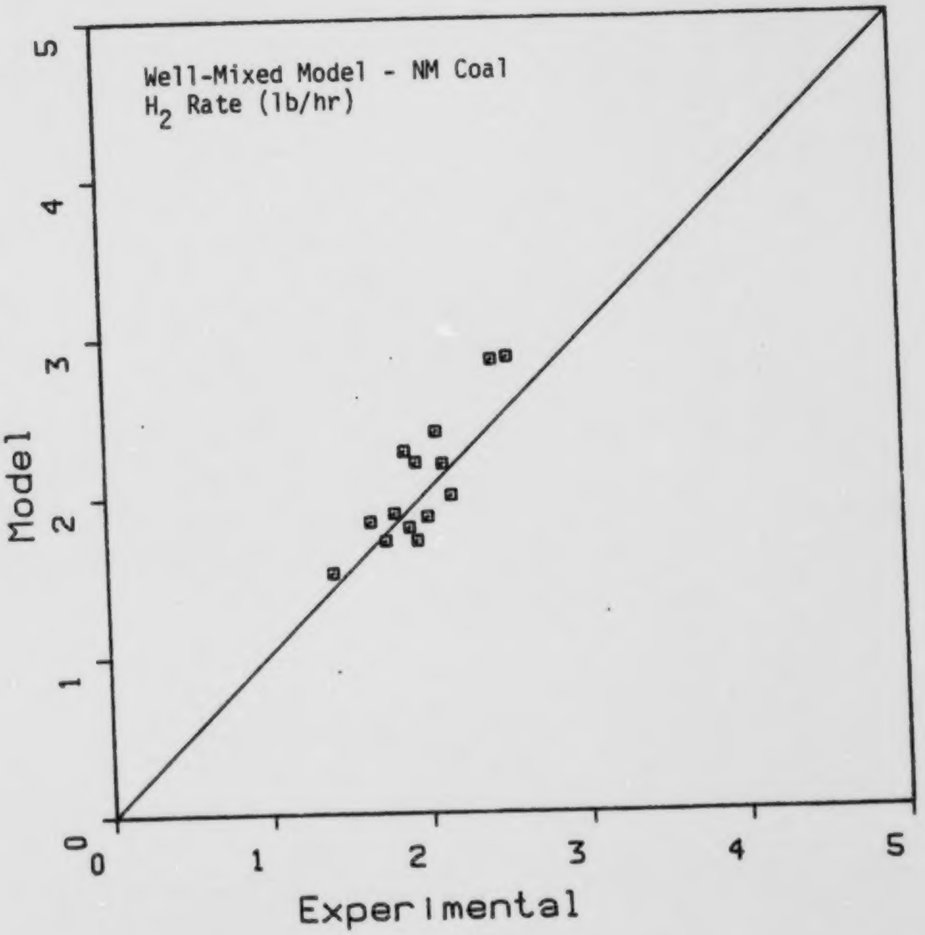

FIGURE 27

PREDICTED VS. EXPERIMENTAL HYDROGEN PRODUCTION RATE FOR NM COAL, WELL-MIXED MODEL

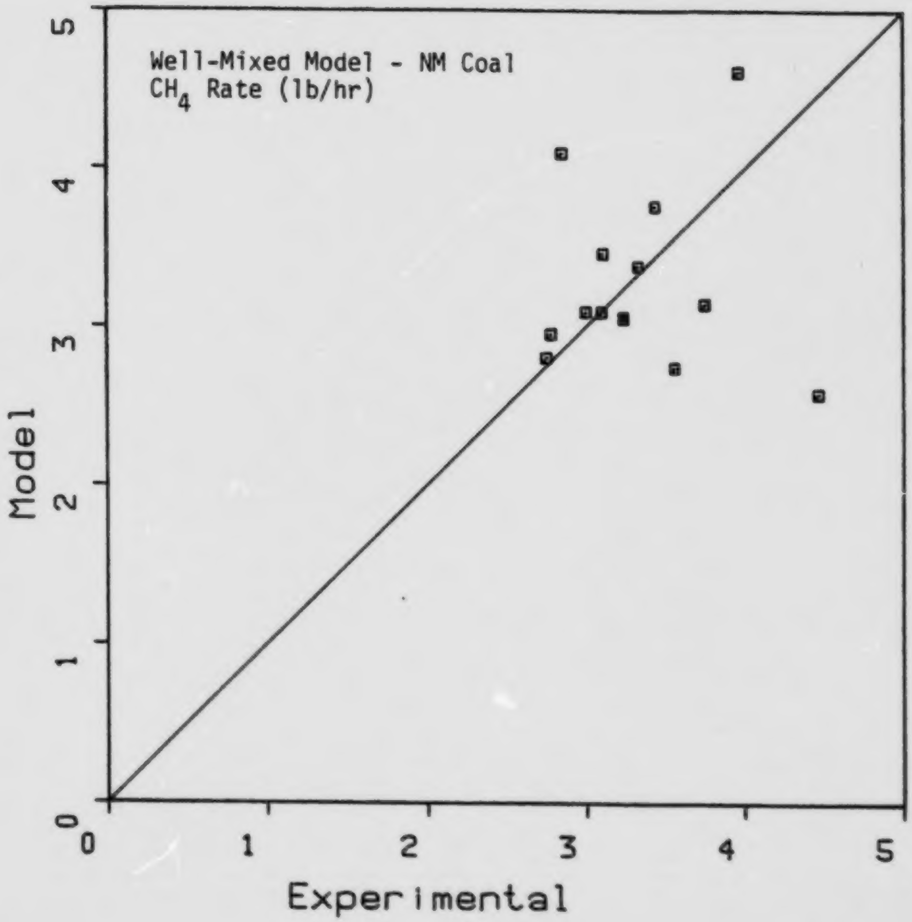

FIGURE 28

PREDICTED VS. EXPERIMENTAL METHANE PRODUCTION RATE FOR NM COAL, WELL-MIXED MODEL

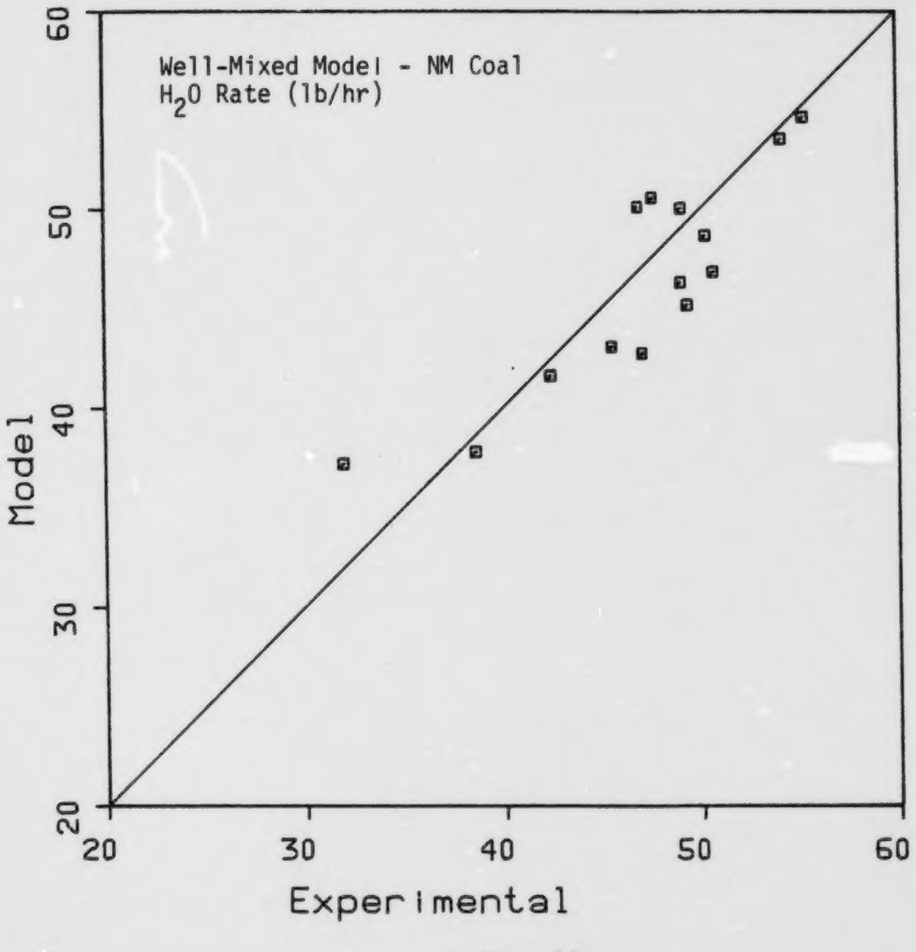

FIGURE 29

PREDICTED VS. EXPERIMENTAL WATER EVOLUTION RATE
FOR NM COAL, WELL-MIXED MODEL

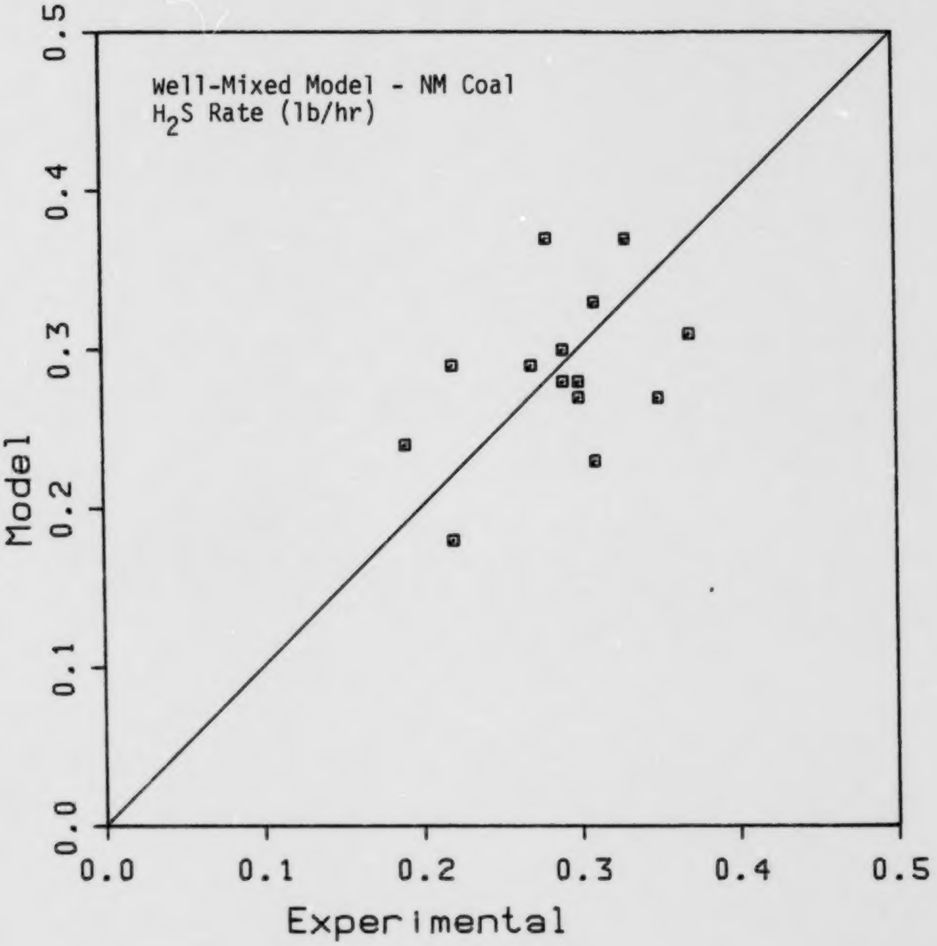

FIGURE 30

PREDICTED VS. EXPERIMENTAL HYDROGEN SULFIDE PRODUCTION RATE FOR NM COAL, WELL-MIXED MODEL

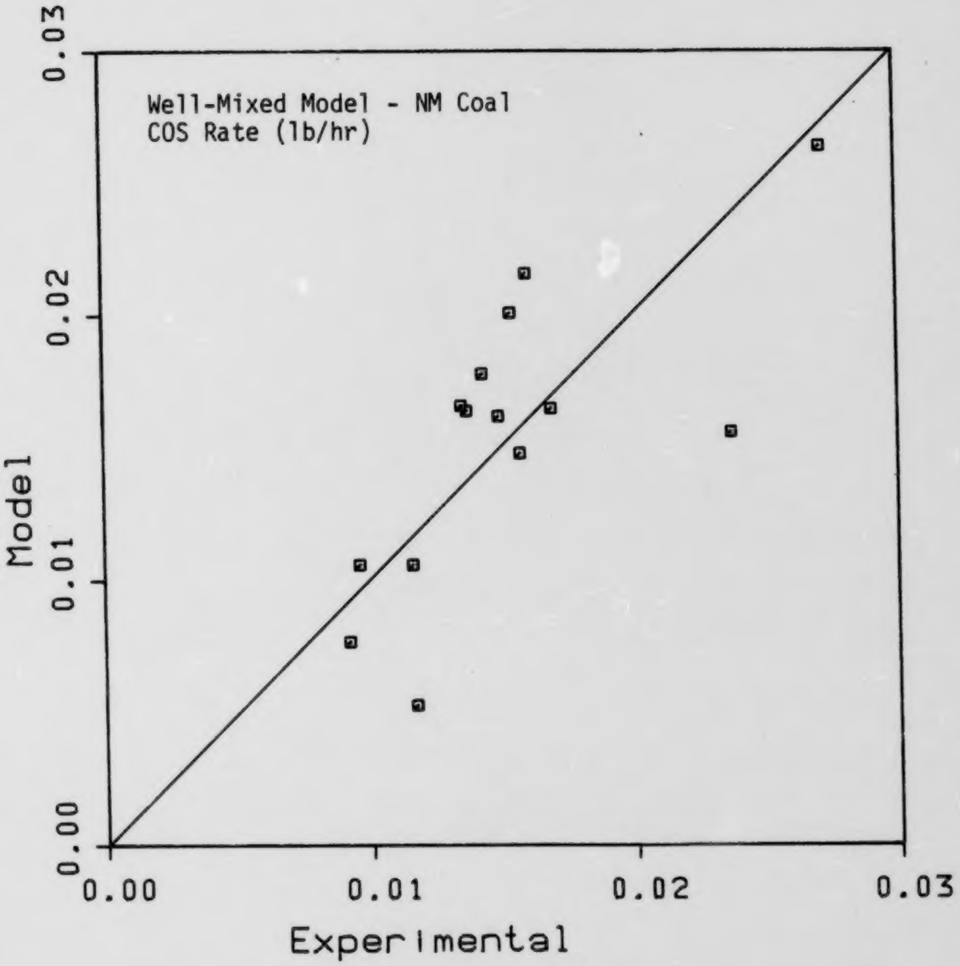

FIGURE 31

PREDICTED VS. EXPERIMENTAL CARBONYL SULFIDE PRODUCTION RATE FOR NM COAL, WELL-MIXED MODEL

COS. The agreement is reasonably good for the species CO, CO_2, H_2, and H_2O. The data in Figure 25 for CH_4 are scattered, but the scatter is evenly distributed about the 45^o line. The sulfur gas parity plots also show a considerable degree of scatter about the 45^o line. Considering the small flow rates involved, the agreement is quite good. In addition, the predicted and measured tar production rates showed fair agreement.

For each run, the water-gas shift equilibrium ratio was calculated from both experimental measurements and model predictions of the gas composition. A plot of the predicted vs experimental values of this ratio is given in Figure 32. The substantial degree of scatter may be attributed to the simplicity of the model, and equally to the fact that the mole fractions which are the constituents of K_{wg} are interdependent, so that an experimental error in one of them affects the values of the others.

The significance of this plot emerges when it is compared with Figure 33, which shows the values of K_{wg} predicted assuming shift equilibrium. This assumption leads to overprediction of K_{wg} and lends support to the conclusion that the shift reaction should not be assumed to proceed to equilibrium.

TWO-PHASE MODEL RESULTS

The two-phase bubbling-bed model of the gasifier contains the same three parameters as the well-mixed model. In addition, a fourth parameter -- the char abrasion constant -- is required to calculate the particle size reduction due to abrasion in the fluidized bed. All are properties of the material being gasified. The parameters are independent of processing conditions, and once determined they are applicable to any set of reactor conditions. The adjustable parameters for the two-phase model are:

1. The char reactivity parameter, f_0
2. The CO/CO_2 combustion product coefficient, a
3. The shift reactivity factor, f_{wg}
4. The char abrasion constant, k_a

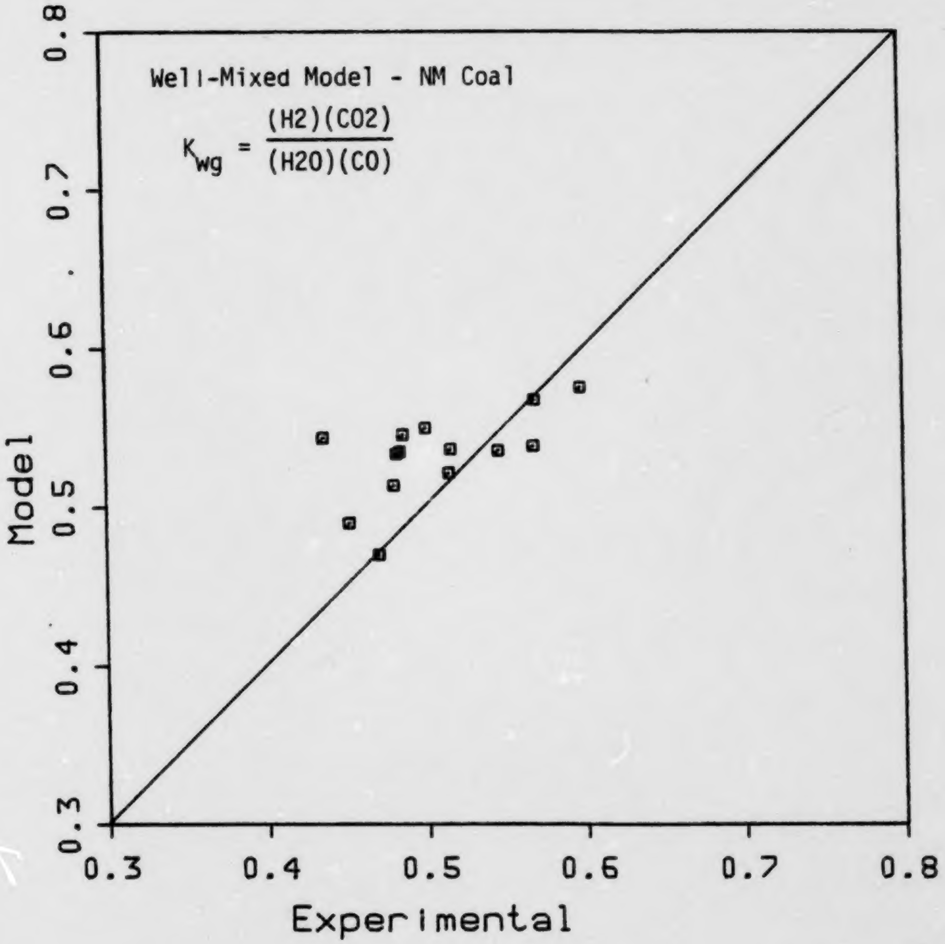

FIGURE 32

PREDICTED VS. EXPERIMENTAL K_{WG} VALUE FOR NM COAL, WELL-MIXED MODEL

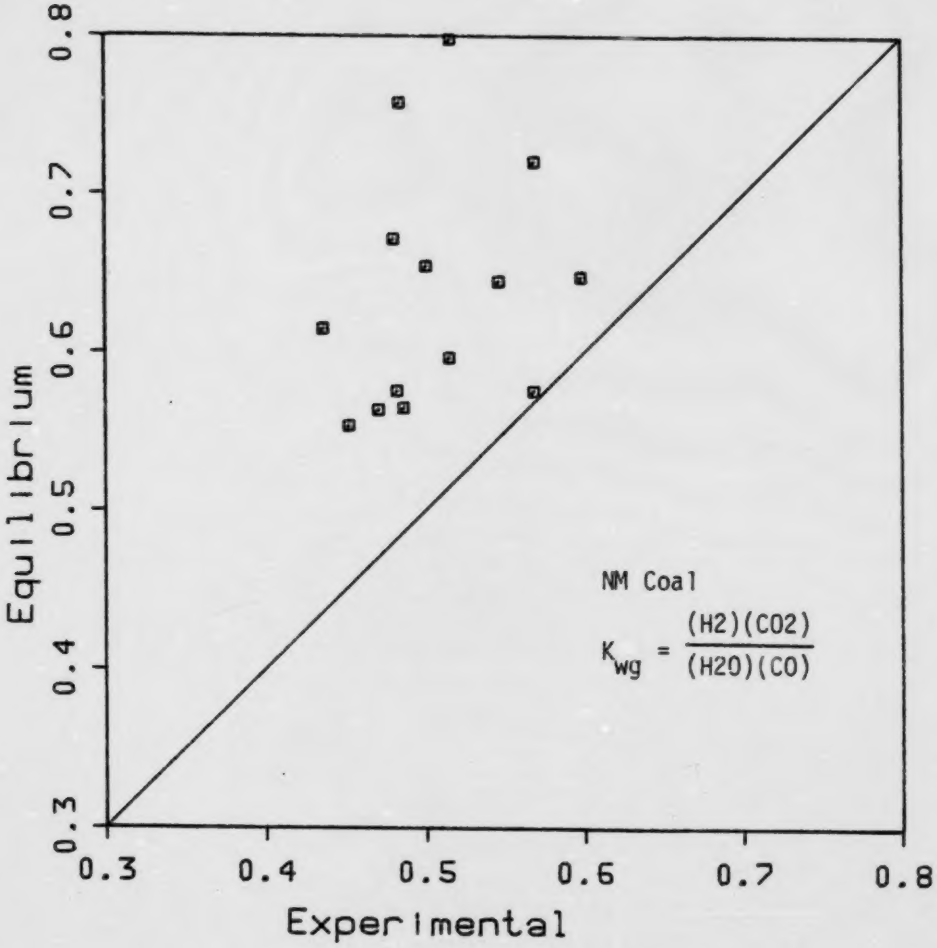

FIGURE 33

EQUILIBRIUM VS. EXPERIMENTAL K_{WG} VALUE FOR NM COAL

The two-phase bubbling-bed model of the gasifier is a much more complex model than the well-mixed model. It also requires a much larger program and greater computer time for completion. As a consequence of the model's size and limited available computing time, the optimization procedure was less detailed than that for the well-mixed model. To speed the optimization computations, the step sizes used in searching for the optimal set of parameter values were increased from those used in optimizing the well-mixed model parameters, and smaller data bases were used.

The modeling options used during the optimization procedures were: specified temperature profile from experimental measurements, jetting, elutriation, water gas kinetics, and equality of the sulfur and carbon conversions. The objective function that was used in optimization of the well-mixed model was modified in the following manner:

$$Y' = Y + 0.1[(e_p - e_m)/e_m]^2 \qquad (165)$$

Y is given by equation (158), e_p is the predicted elutriation rate, and e_m is the experimentally measured rate. The additional term was added to aid in the evaluation of the char abrasion constant, k_a.

Kentucky Bituminous Char

Four runs were chosen to form the data base for optimization of the parameters for the Kentucky char (Purdy (1983)). The resulting optimal parameter values were:

$$f_o = 0.80 \qquad (166)$$
$$a = 1.00 \qquad (167)$$
$$f_{wg} = 1.5\times10^{-4} \qquad (168)$$
$$k_a = 3.0\times10^{-4} \qquad (169)$$

The values of f_o, a, and f_{wg} are all higher than the corresponding values determined for the well-mixed model. The differences may be due to the gas-solid contacting assumed in the two models. In the two-phase model, a large fraction of the gas passing through the bed is in the bubble phase and does not contact the coal. The well-mixed model does not allow for such gas bypassing, and as a consequence may underpredict the reactivity parameter values.

Using the optimal parameter values, the model was run for the conditions of all accepted Kentucky char runs. The model predictions for carbon conversion and gas production are plotted versus the experimental results in Figures 34 and 35. The plots show good agreement between the model predictions and the experimental measurements. The quality of the correlations are similar to those obtained with the well-mixed model (Figures 16 and 17).

Correlation plots for the production rates of the gaseous products H_2, CO, and CO_2 are shown in Figures 36-38. The plots show considerable scatter; however, the points show a reasonable proximity to the 45^o line.

To obtain a quantitative measure of the model's ability to correlate the Kentucky char data, Y -- given by equation (158) -- was evaluated using all experimental runs in the data base. Y, a normalized sum of squared errors between model prediction and experimental measurements, was also evaluated for the well-mixed model. The results were Y=0.069 for the two-phase model and Y=0.047 for the well-mixed model. The results indicate that the well-mixed model does a slightly better job of correlating run data than does the two-phase model. The quantity Y could probably be reduced for the two-phase model by performing a more detailed optimization for the model parameters.

New Mexico Subbituminous Coal

The optimization routine was ran to determine the optimal parameter values. The data base for optimization was composed of runs GO-68, 69B, 78, and 84. The optimization procedure yielded the following results:

$$f_o = 8.60 \qquad (170)$$
$$a = 1.00 \qquad (171)$$
$$f_{wg} = 2.2\times10^{-4} \qquad (172)$$
$$k_a = 4.5\times10^{-4} \qquad (173)$$

The char reactivity factor for the New Mexico coal is roughly 11 times greater than that for the Kentucky char. This agrees with the experimentally observed trend, and with the results of the well-mixed model (f_o ratio of 15). The combustion product coefficient is the same as that determined for the Kentucky char, and indicates that CO_2 is the sole product of the carbon-oxygen reaction. Similar values were obtained for the shift reactivity factor, while the greater abrasion constant value for the New Mexico coal indicates that it is a more friable material than the Kentucky char.

Using the above values, the model was used to correlate the results for New Mexico coal. Parity plots of the main reactor performance variables are shown in Figures 39-44. In general, reasonable agreement was attained between the model predictions and experimental results.

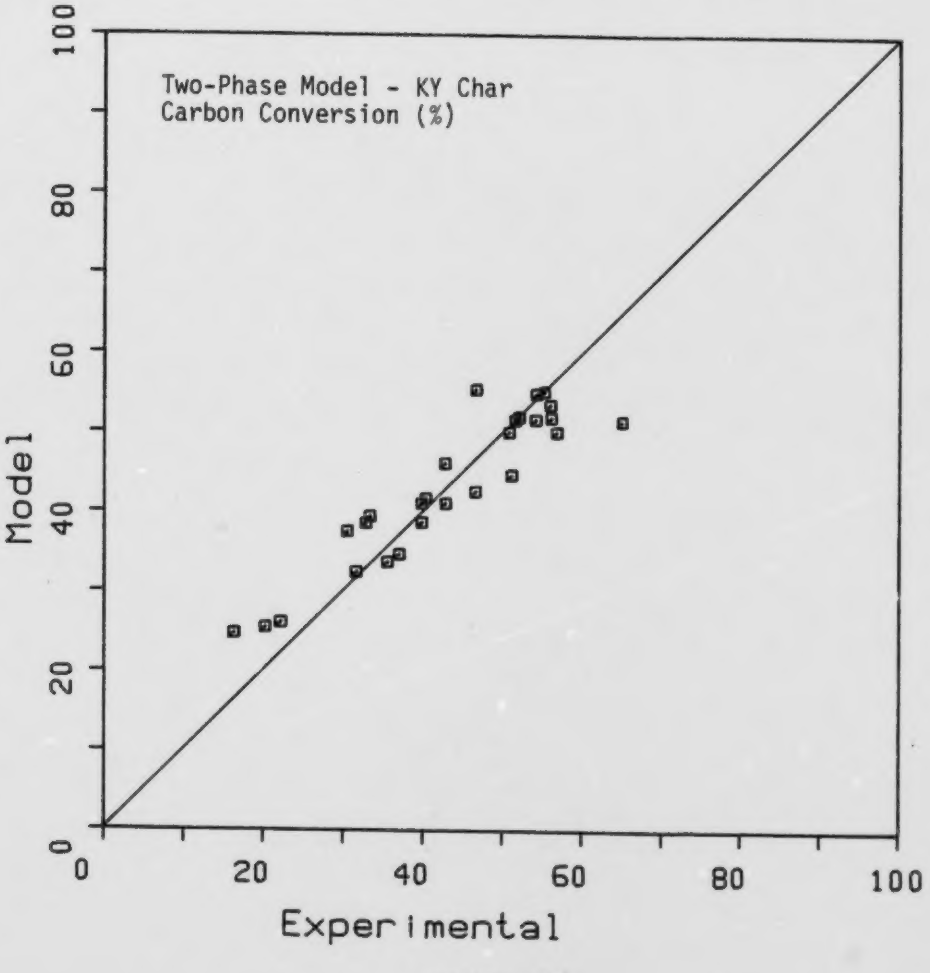

FIGURE 34

PREDICTED VS. EXPERIMENTAL CARBON CONVERSION
FOR KY CHAR, TWO-PHASE MODEL

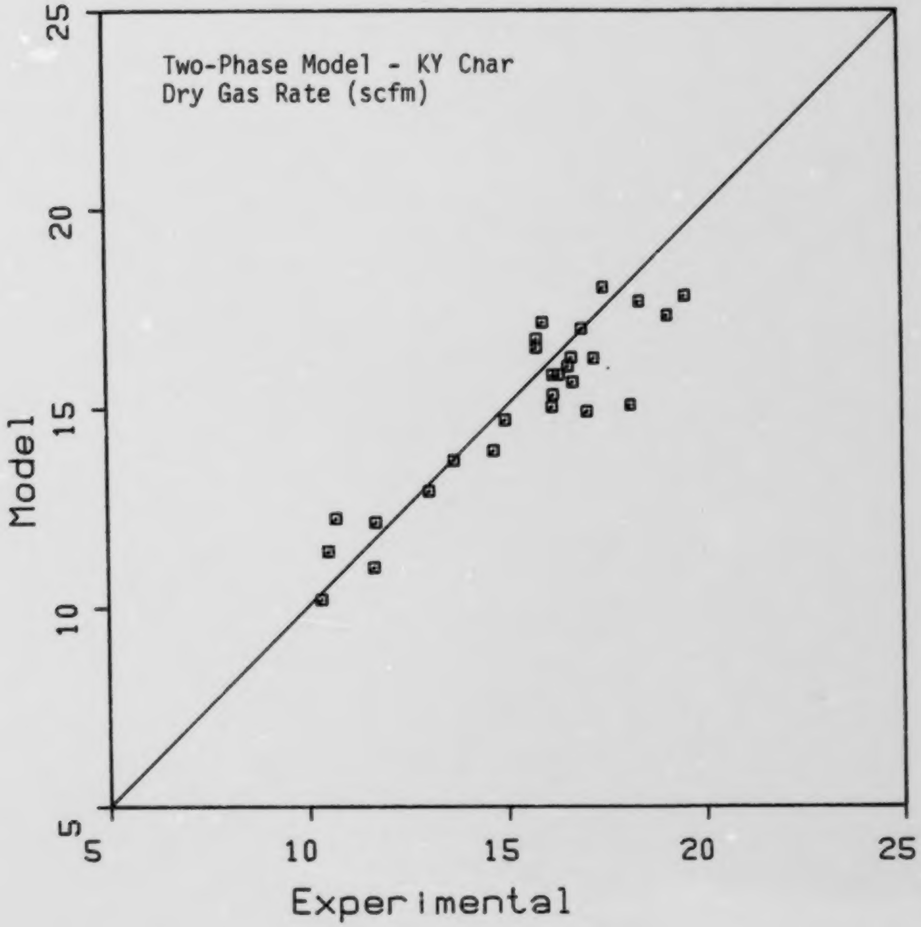

FIGURE 35

PREDICTED VS. EXPERIMENTAL GAS PRODUCTION RATE FOR KY CHAR, TWO-PHASE MODEL

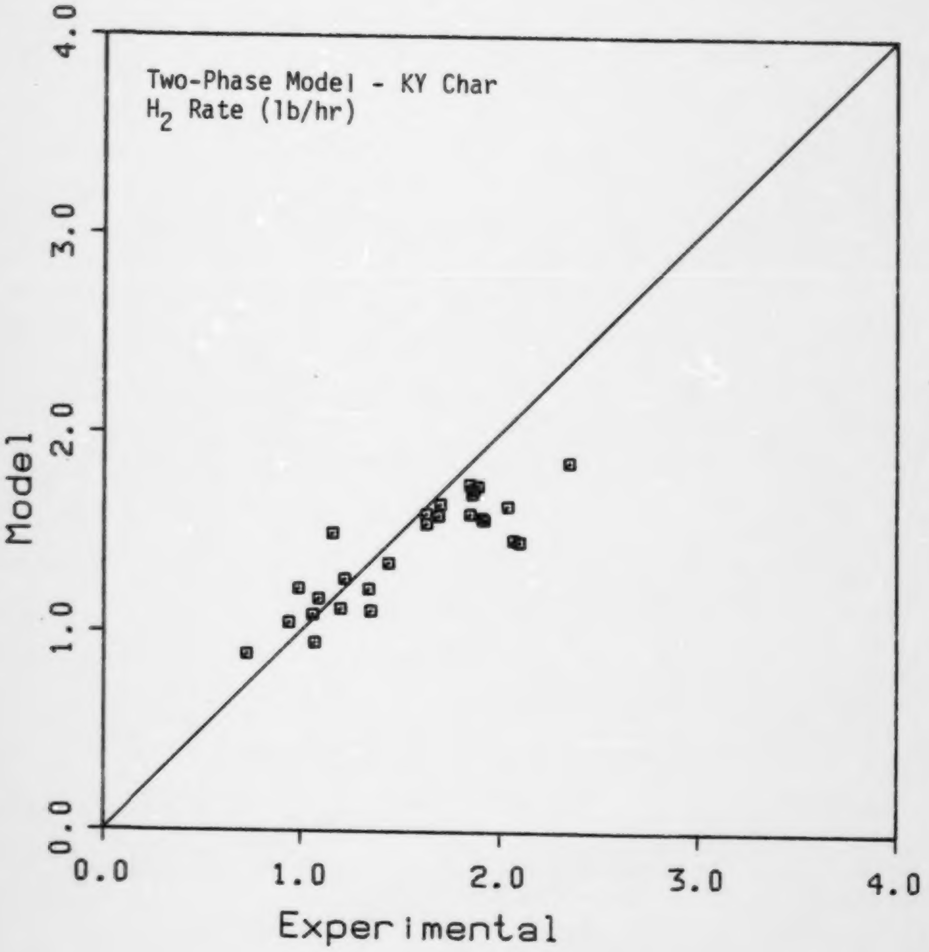

FIGURE 36

PREDICTED VS. EXPERIMENTAL HYDROGEN PRODUCTION RATE
FOR KY CHAR, TWO-PHASE MODEL

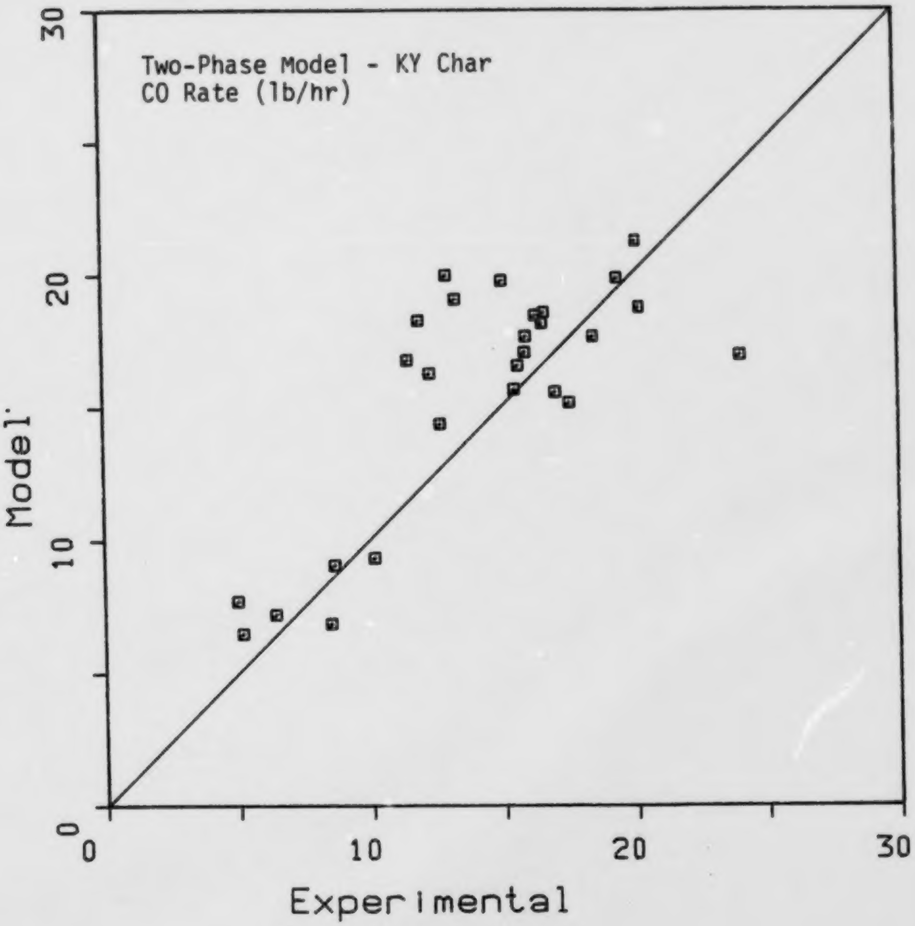

FIGURE 37

PREDICTED VS. EXPERIMENTAL CARBON MONOXIDE PRODUCTION RATE FOR KY CHAR, TWO-PHASE MODEL

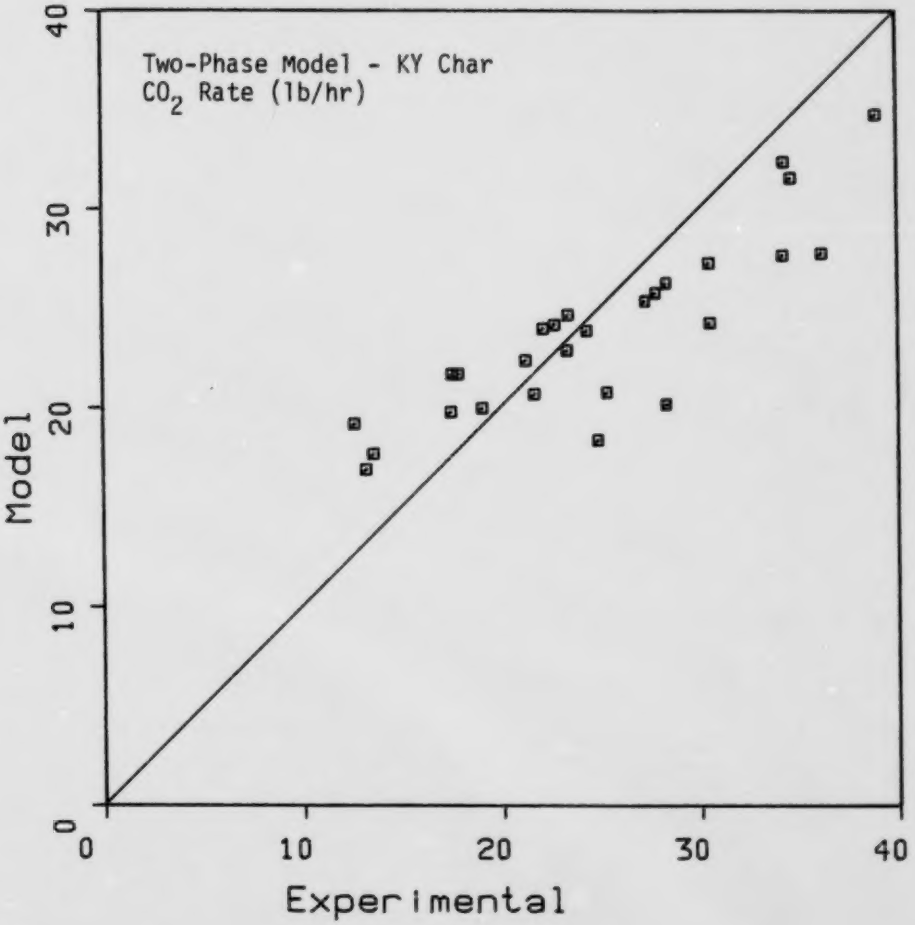

FIGURE 38

PREDICTED VS. EXPERIMENTAL CARBON DIOXIDE PRODUCTION RATE FOR KY CHAR, TWO-PHASE MODEL

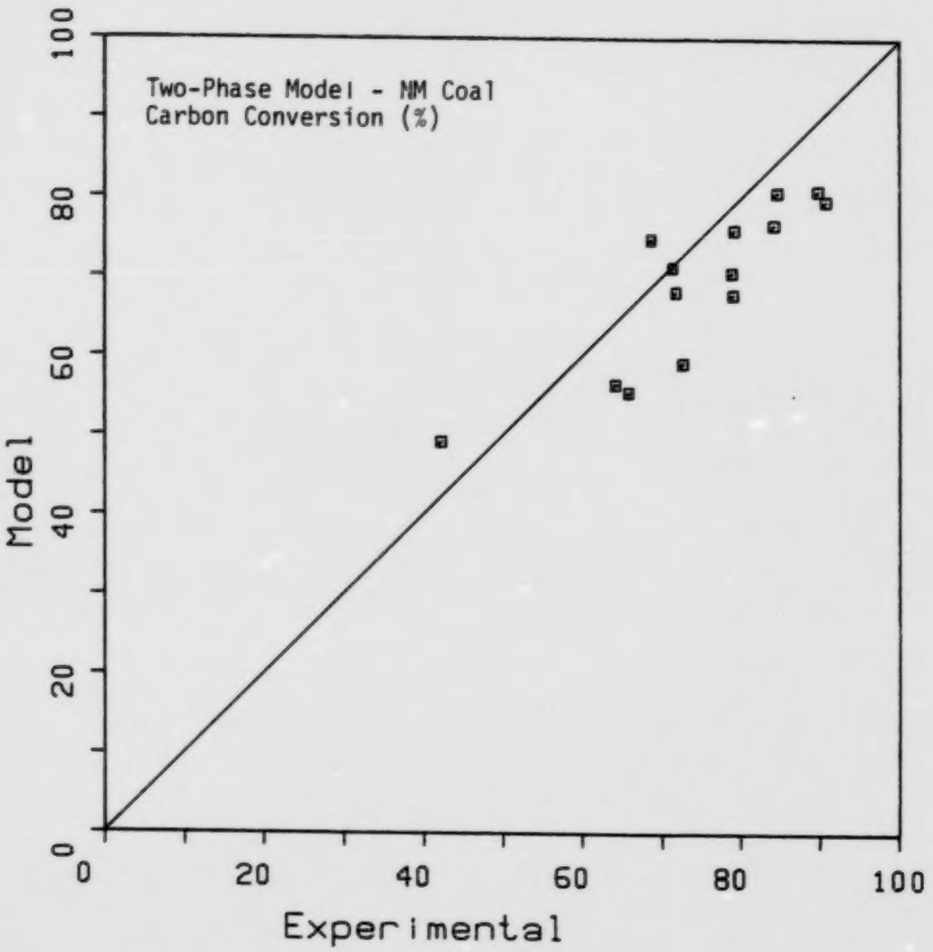

FIGURE 39

PREDICTED VS. EXPERIMENTAL CARBON CONVERSION FOR NM COAL, TWO-PHASE MODEL

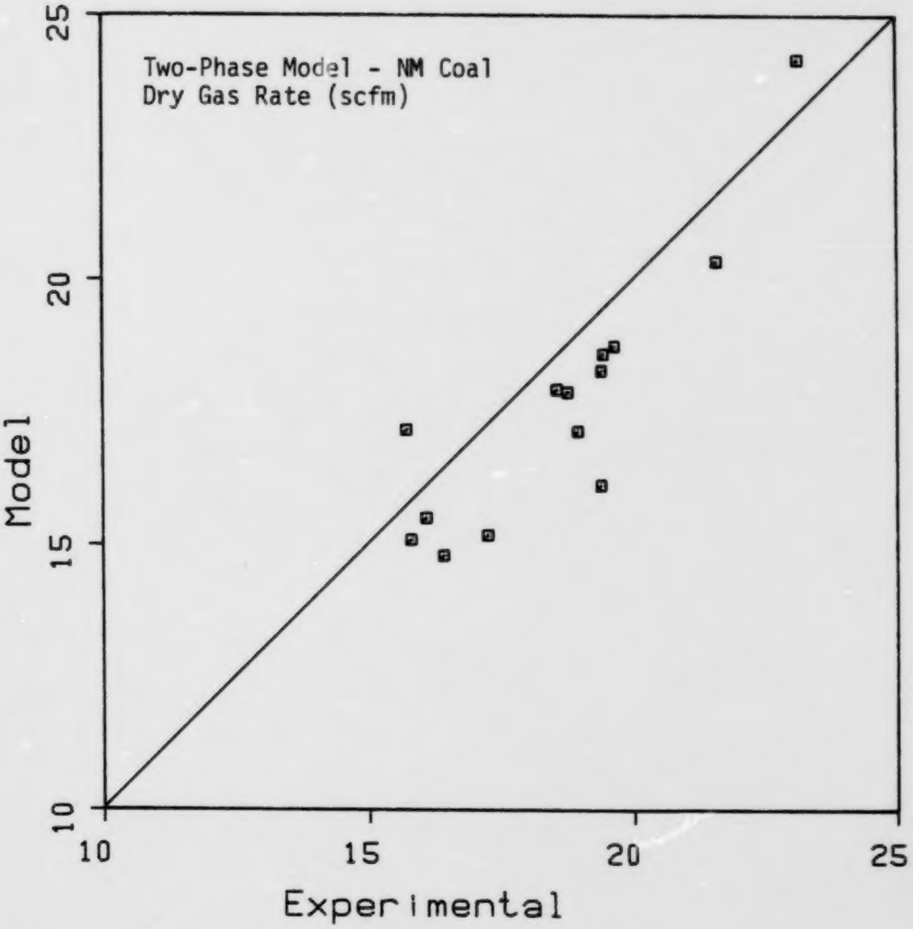

FIGURE 40

PREDICTED VS. EXPERIMENTAL GAS PRODUCTION RATE FOR NM COAL, TWO-PHASE MODEL

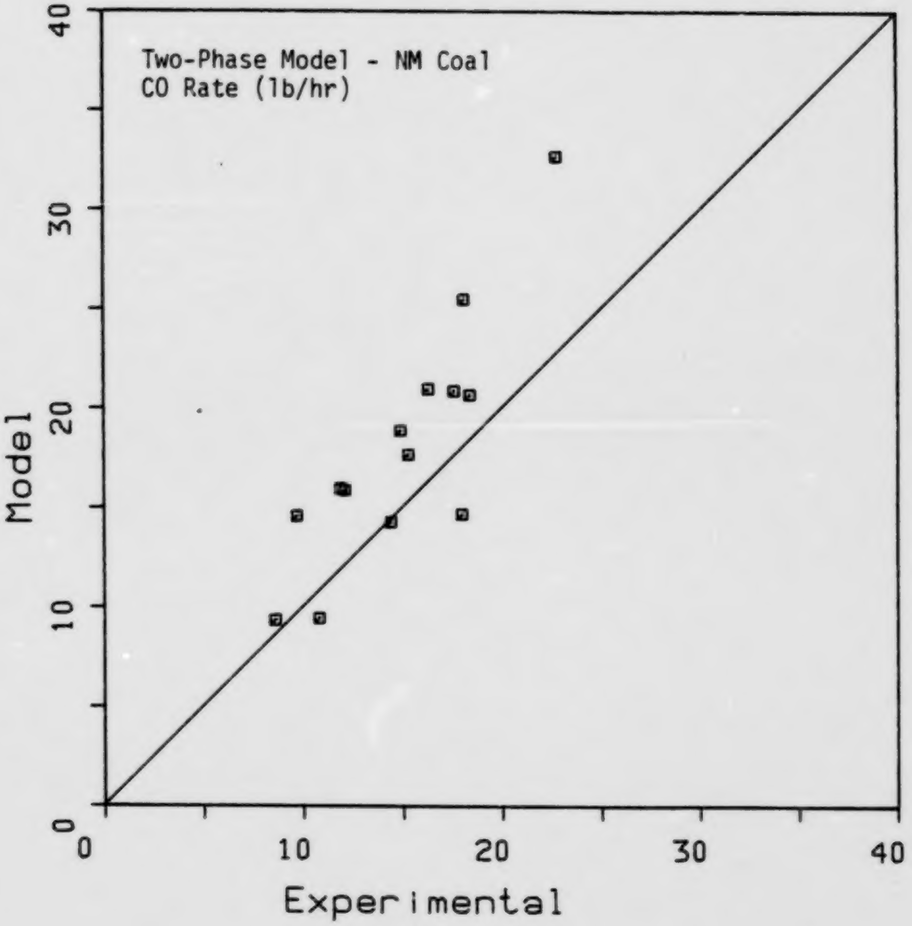

FIGURE 41

PREDICTED VS. EXPERIMENTAL CARBON MONOXIDE PRODUCTION RATE FOR NM COAL, TWO-PHASE MODEL

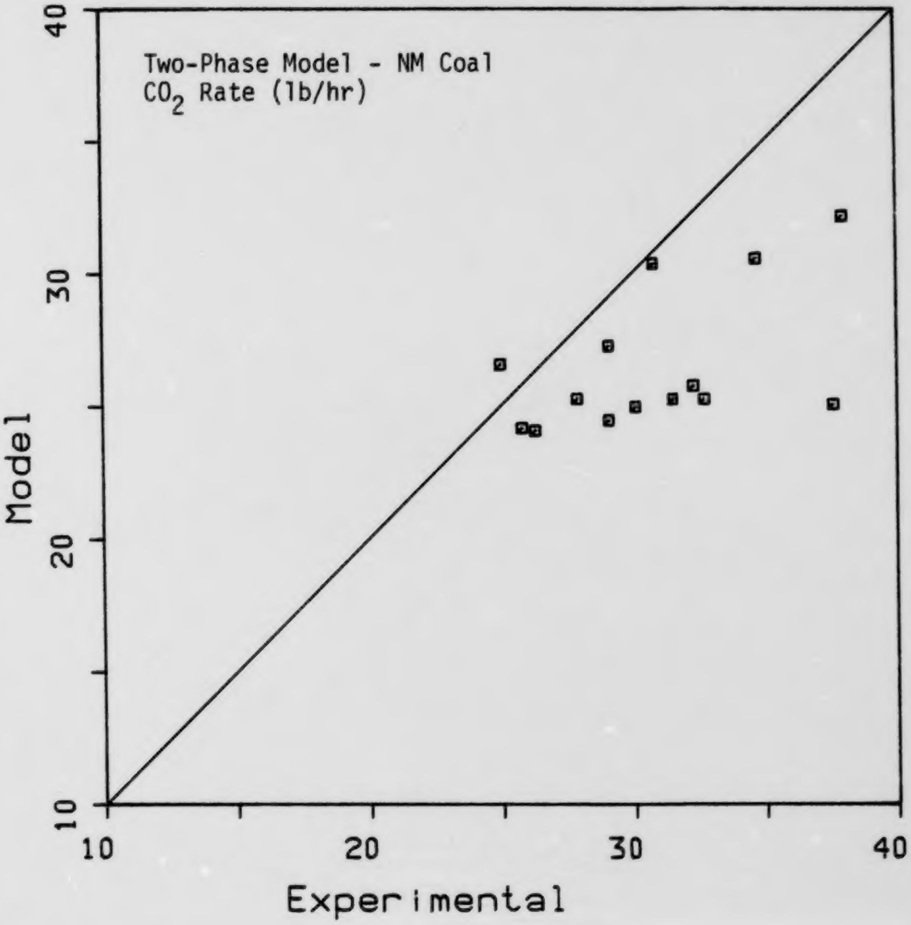

FIGURE 42

PREDICTED VS. EXPERIMENTAL CARBON DIOXIDE PRODUCTION RATE FOR NM COAL, TWO-PHASE MODEL

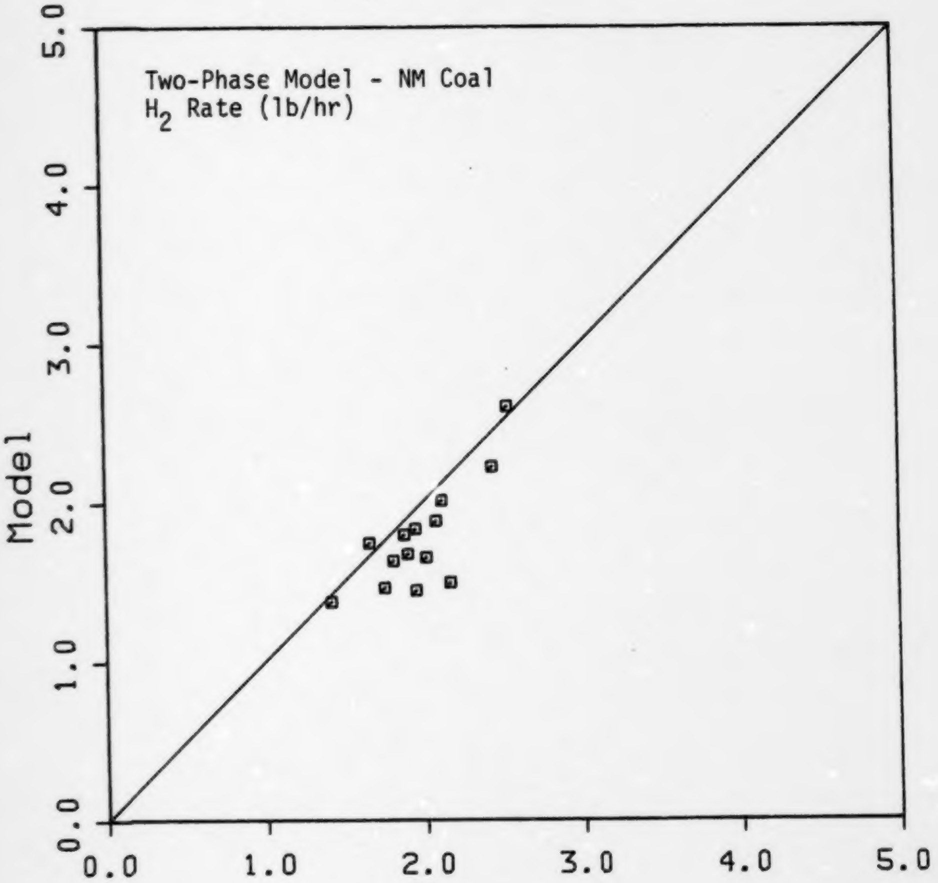

FIGURE 43

PREDICTED VS. EXPERIMENTAL HYDROGEN PRODUCTION RATE
FOR NM COAL, TWO-PHASE MODEL

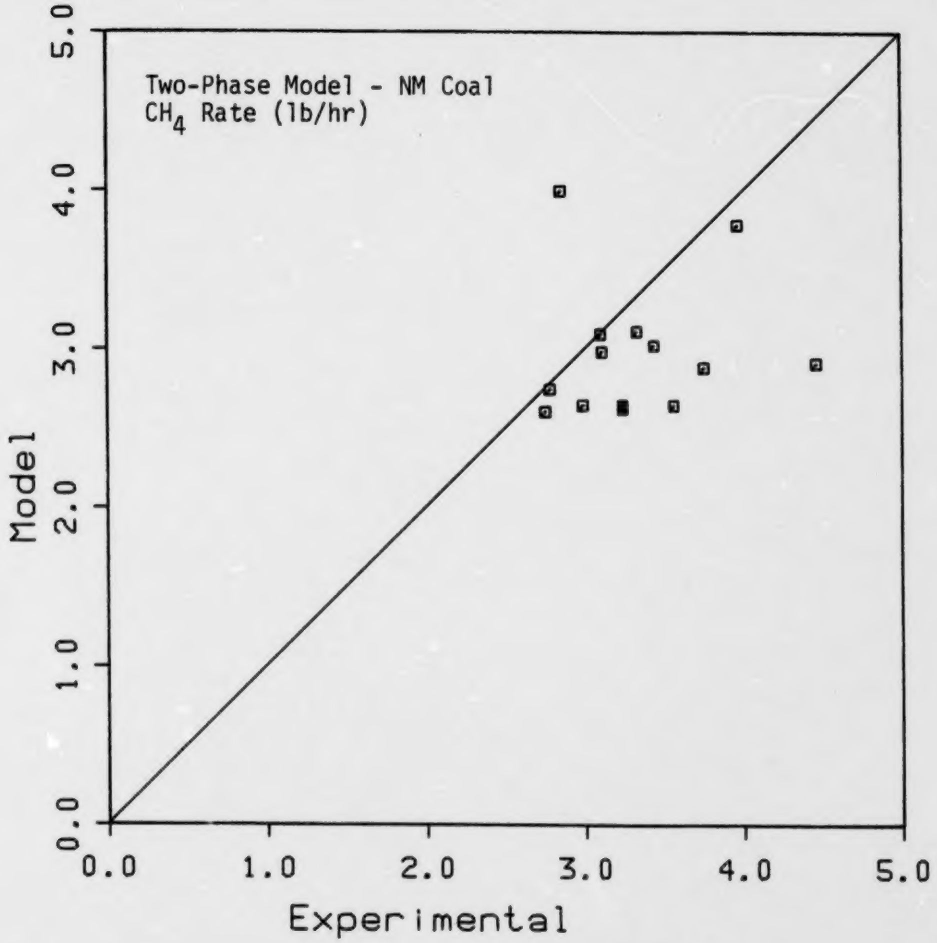

FIGURE 44

PREDICTED VS. EXPERIMENTAL METHANE PRODUCTION RATE FOR NM COAL, TWO-PHASE MODEL

Figures 39 and 40 show the predicted versus experimental carbon conversions and gas production rates. Similar plots for CO, CO_2, H_2, and CH_4 are given by Figures 41-44.

Equation (158), the normalized sum of squared errors between model predictions and experimental measurements, was evaluated for all New Mexico coal run data as done for the Kentucky char. The resulting values of Y were 0.060 for the two-phase model and 0.021 for the well-mixed model. Both Y values are better than the corresponding values obtained for the Kentucky char. Comparison of the two models again shows a better correlation for the well-mixed model. As stated for the Kentucky char, improvement in the results obtained with the two-phase model would probably be achieved by a more refined optimization procedure. It is also expected that incorporation of more sophisticated methods of predicting the devolatilization yields will improve the overall model predictions. Work is currently being conducted using a laminar flow reactor (rapid pyrolysis) that should generate improved devolatilization prediction methods.

Effects of Modeling Options

Several modeling options were built into the two-phase bubbling-bed model. Each was tested to determine its effect on model predictions. The results for each modeling option are discussed in the following sections.

Temperature Specification--

Using experimentally measured temperature profiles, the model was run for each New Mexico coal run. In addition, the model was run using the average bed temperature calculated from the experimental temperature data. Table 18 compares the results from each series of model runs. Table 18 shows that the use of the average bed temperature in modeling leads to conversion and gas production results comparable to those obtained using the experimental temperature profile.

Equation (158) was evaluated using all New Mexico coal runs for the case of an isothermal fluidized bed. A result of Y=0.047 was obtained, which unexpectedly was lower than that obtained when the experimental bed temperature profile was used in modeling (Y=0.060). The experimental temperature measurements most likely represent an average of the gas and solid temperatures. It is possible that the solids temperature varies little with bed position, and that the measured profile is a result of changes in the gas temperature. If correct, the use of an average bed temperature in the model would be more accurate for the solids. This might explain the lower Y value obtained for the case of the isothermal model.

TABLE 18
EFFECT OF TEMPERATURE SPECIFICATION ON MODEL PREDICTIONS

	Temperature Profile		Isothermal	
Run No	% C Conv.	Gas, scfm	% C Conv.	Gas, scfm
GO-66	79.7	18.77	79.1	18.59
68B	74.8	24.18	70.5	22.65
69B	71.3	17.89	68.7	17.04
72	80.8	18.30	79.6	17.99
74	49.2	17.18	49.0	17.04
76	67.9	17.15	66.7	16.86
78	56.5	15.10	57.4	15.26
79	76.0	17.94	75.3	17.72
80B	70.6	15.19	73.5	15.77
81B	59.2	16.14	65.6	17.80
81D	55.5	14.81	57.8	15.39
82	81.0	18.62	80.3	18.29
84	68.2	15.52	67.0	15.25
85B	76.7	20.37	74.8	19.87

To illustrate further the effect of the temperature profile on model predictions, the model was run for a series of runs having the same average bed temperature but different temperature profiles. The profiles are shown in Figure 45. All other operating variables were held constant at the values experimentally measured for run GO-76. The results are given in Table 19. As the temperature drop across the fluidized-bed increases, carbon conversion and gas production increase. The H_2, CO, and H_2S contents in the dry gas increase with increasing temperature difference, and CO_2 and CH_4 decrease.

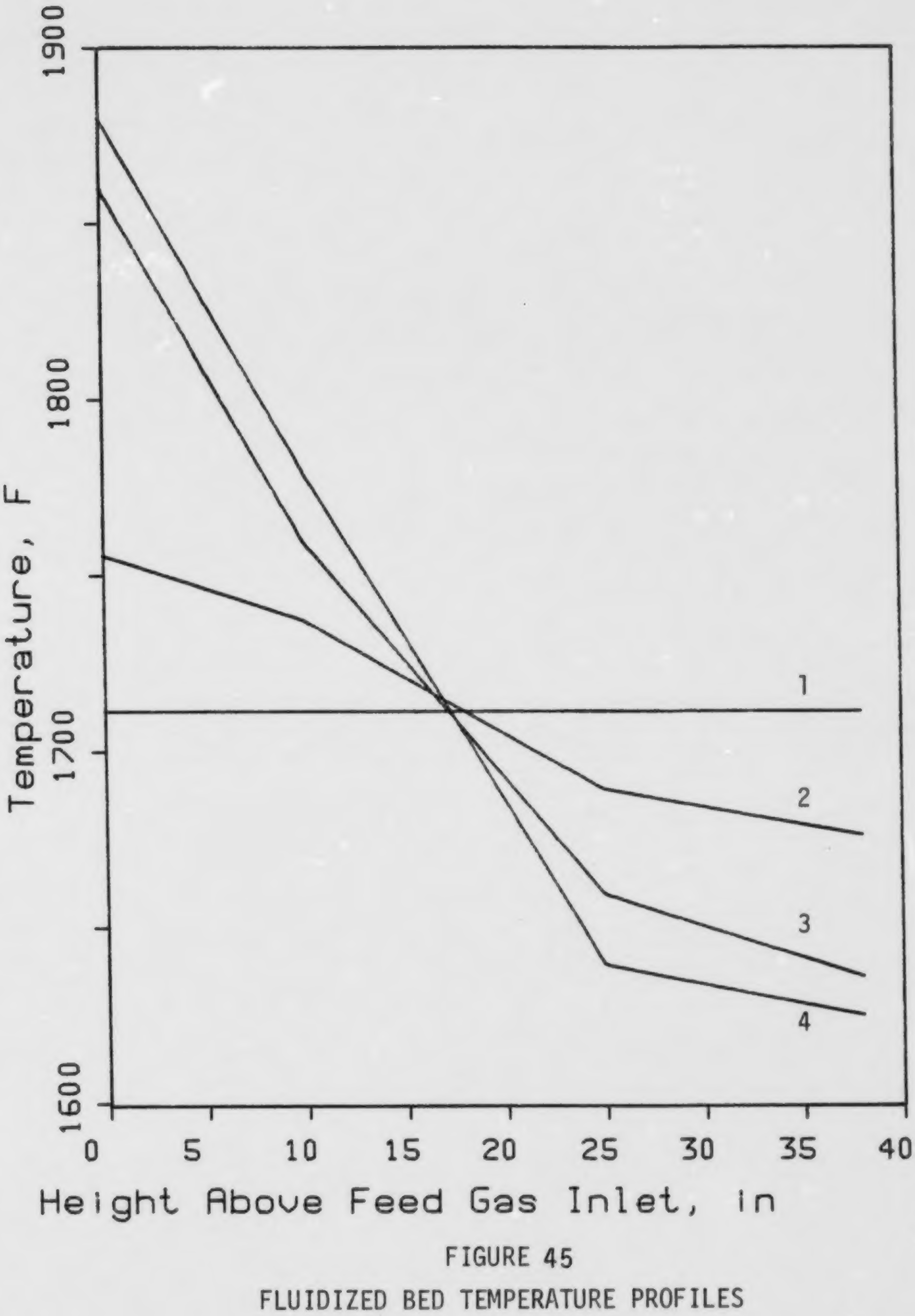

FIGURE 45
FLUIDIZED BED TEMPERATURE PROFILES

TABLE 19
EFFECT OF TEMPERATURE PROFILE ON MODEL PREDICTIONS

	Temperature Profile (from Figure 79)			
	1	2	3	4
% C Conversion	66.7	67.9	73.1	74.7
Dry Make Gas Rate, scfm	16.86	17.15	18.77	19.19
Gas Composition, Dry Mole %				
H_2	28.40	28.71	31.46	31.87
CO	21.28	22.09	22.46	23.34
CO_2	20.57	20.07	19.68	19.01
CH_4	7.03	6.79	5.97	5.78
H_2S	0.28	0.29	0.29	0.30

The modeling results for various temperature profiles indicate that for the operating conditions of the NCSU gasifier, the use of an average bed temperature in modeling is a reasonable simplification. For the experimental runs using New Mexico subbituminous coal as the feedstock, there were no significant differences between model predictions using an average temperature and those using the experimental temperature profile. However, for extreme temperature drops across the fluidized bed, large discrepancies between model predictions may occur.

Jetting--

The model was run with and without consideration of a jetting region at the gas inlet for the New Mexico coal gasification runs. The results were compared to determine to the effect of the jetting region on model predictions. The main reactor performance variables, carbon conversion and make gas production rate, are compared in Table 20 for the two cases. The results indicate that inclusion of a jetting region has a small effect on model predictions. For the runs in Table 20, consideration of a jetting region yielded slightly higher conversion and gas production rate predictions. The differences are small and show that little is gained from the added complexity of consideration of a jetting region.

TABLE 20
EFFECT OF JETTING REGION ON MODEL PREDICTIONS

	Include Jetting		Neglect Jetting	
Run	% C Conv.	Gas, scfm	% C Conv.	Gas, scfm
GO-66	79.7	18.77	78.6	18.36
68B	74.8	24.18	72.7	23.36
69B	71.3	17.89	69.9	17.50
72	80.8	18.30	79.7	17.96
74	49.2	17.18	48.5	16.83
76	67.9	17.15	67.4	17.22
78	56.5	15.10	55.6	14.84
79	76.0	17.94	74.4	17.50
80B	70.6	15.19	69.3	14.82
81B	59.2	16.14	58.3	15.79
81D	55.5	14.81	55.1	14.60
82	81.0	18.62	80.4	18.30
84	68.2	15.52	67.7	15.59
85B	76.7	20.37	74.6	19.71

As a quantitative measure of the effect of the jetting region on model predictions, equation (158) was evaluated for the cases of jetting and no jetting. The calculated values of Y showed no significant difference, as Y=0.060 was obtained when jetting was was considered, and Y=0.058 was obtained when jetting was neglected.

The model was also run for a hypothetical set of conditions for which consideration of a jetting region would be expected to be of most importance. A shallow bed (6 in), high feed gas rates (32 scfm H_2O, 21 scfm N_2, and 3.3 scfm O_2), and high reactivity (f_0=10.6) were used as inputs. For this case, the model predictions with consideration of jetting were 61.4% carbon conversion and 15.9 scfm dry N_2-free make gas. The results were 56.5% carbon conversion and 14.3 scfm make gas when jetting was neglected. The differences in model predictions for this case are greater than those for the New Mexico coal runs, but are not excessive. The results indicate that for most conditions the jetting region in fluidized bed gasification can be neglected without serious effects on model predictions.

Elutriation--

A model option allows for the consideration of elutriation. The model was run for the set of gasifier runs using New Mexico coal as the feed to determine the effect of elutriation on the model predictions. Table 21 gives the results for carbon conversion and gas production. As can be seen, the inclusion of elutriation in the model has a minimal effect on the predicted conversion and gas production rate. The results for the production rates of individual gaseous effluents showed no major differences between the two models.

Equation (158) was evaluated for the case of no elutriation, and a result of Y=0.062 was obtained. The Y value when elutriation is considered is only slightly better at 0.060. The results indicate that there are no major differences in model predictions of conversion and gas production rates between the two cases of the two-phase model.

TABLE 21
EFFECT OF ELUTRIATION CONSIDERATION ON MODEL PREDICTIONS

	Elutriation		No Elutriation	
Run	% C Conv.	Gas, scfm	% C Conv.	Gas, scfm
GO-66	79.7	18.77	80.3	18.90
68B	74.8	24.18	75.5	24.39
69B	71.3	17.89	71.7	17.96
72	80.8	18.30	81.1	18.37
74	49.2	17.18	49.4	17.21
76	67.9	17.15	68.3	17.23
78	56.5	15.10	56.6	15.12
79	76.0	17.94	76.4	18.02
80B	70.6	15.19	70.7	15.20
81B	59.2	16.14	59.2	16.14
81D	55.5	14.81	55.5	14.82
82	81.0	18.62	81.5	18.71
84	68.2	15.52	68.6	15.59
85B	76.7	20.37	76.9	20.41

The predicted spent char rates and elutriate rates are plotted against the experimental results in Figures 46 and 47. The predicted versus experimental spent char rates of Figure 46 show a large degree of scatter, but it appears that the correlation is better when elutriation is considered in the model. Both models show a tendency to overpredict the spent char rates. The data shown in Figure 47 also shows substantial scatter; however, the scatter appears to be equally distributed about the 45° line. The elutriation correlation is highly dependent on the particle density and size distribution. A large portion of the error between predicted and experimental elutriation rates may be due to inaccuracies in the measured feed particle density and size distribution. The calculations to predict the change in size and density during gasification may also introduce errors. In addition, it is possible that the correlation, developed from combustion data, may

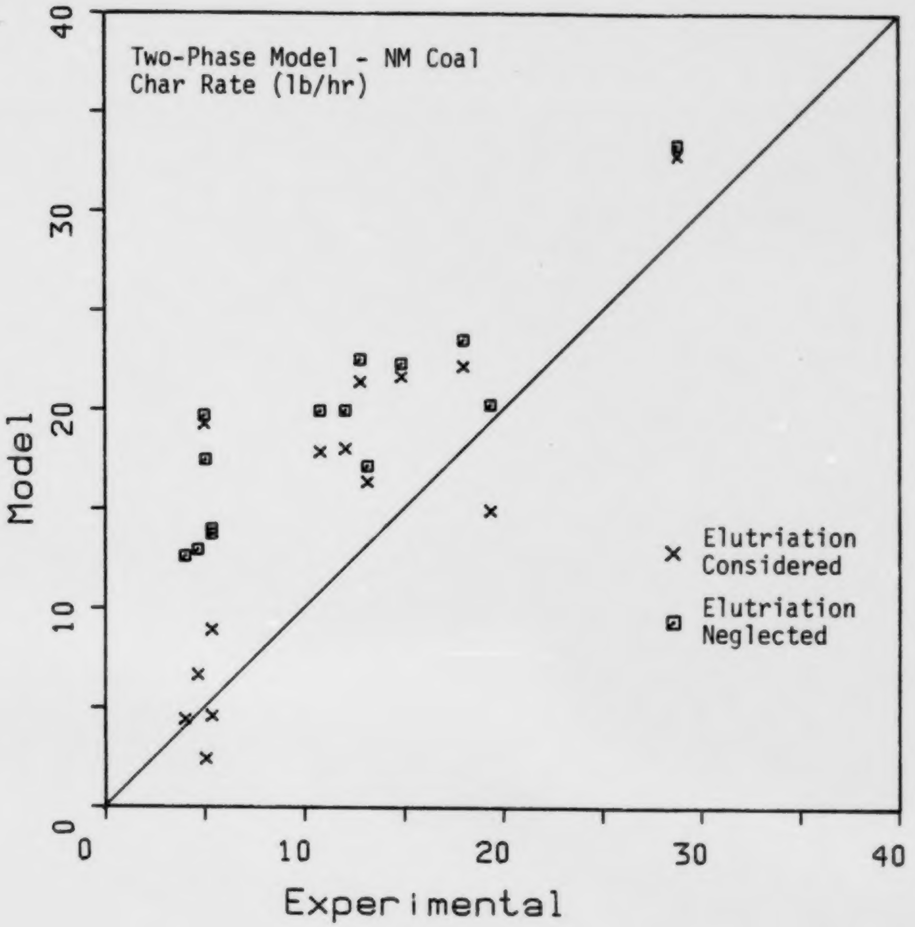

FIGURE 46

PREDICTED VS. EXPERIMENTAL CHAR RATES
FOR NM COAL, TWO-PHASE MODEL

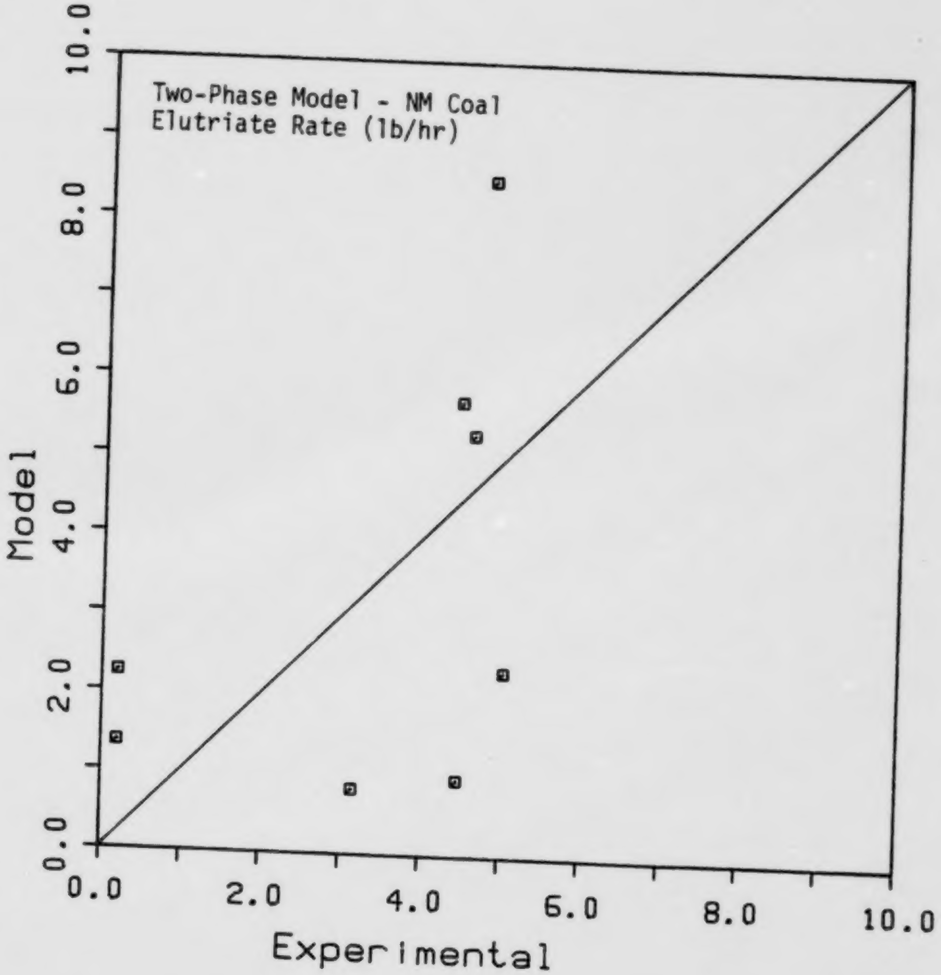

FIGURE 47

PREDICTED VS. EXPERIMENTAL ELUTRIATION RATE
FOR NM COAL, TWO-PHASE MODEL

not be applicable to gasification conditions.

Sulfur Gas Production--

Hydrogen sulfide production can be predicted in two manners: assumption of carbon and sulfur conversion equality, or use of Yergey-Vestal sulfur kinetics (equations (43)-(52)). For both manners of determining H_2S production, the production rate of COS is calculated by assuming equilibrium of the sulfur gas shift reaction (equation 149). The predicted H_2S production rates for both methods are plotted versus the experimentally measured H_2S production rate in Figure 48. There is substantial scatter in the data; however, it can be seen that the assumption of equal sulfur and carbon conversions yields a better correlation than does the use of sulfur kinetics, which leads to underprediction of the H_2S production rate. The Yergey-Vestal sulfur kinetics are strongly dependent on the sulfur form distribution. It is likely that the assumptions made concerning the sulfur form distribution following devolatilization are inaccurate. Improved methods of estimating the distribution would probably result in improved H_2S predictions.

The production rates of the sulfur species are small relative to the other species considered by the model. As a result, the method chosen to determine H_2S production has a negligible effect on the predicted carbon conversion, make gas rate, and production rates of the major species.

EFFECT OF OPERATING VARIABLES

The well-mixed and two-phase gasifier models were run for several sets of hypothetical reactor conditions to determine the effects of selected operating variables on reactor performance. The variables examined were temperature, pressure, H_2O/C feed ratio, solid-phase space time, and feed particle size distribution. The effects of each are discussed in the following sections.

Temperature

A moderate temperature run was chosen to provide the data base for determining the predicted effects of the average bed temperature. The temperature was varied from 1400 to 1900°F, holding all other conditions constant. The resulting feed gas velocity varied from 0.92 to 1.17 ft/s, which is within the experimental operating range. Figures 49 and 50 show the effects of the average bed temperature on carbon conversion and make gas production. As would be expected, both conversion and gas production increase with increasing temperature. Both figures show

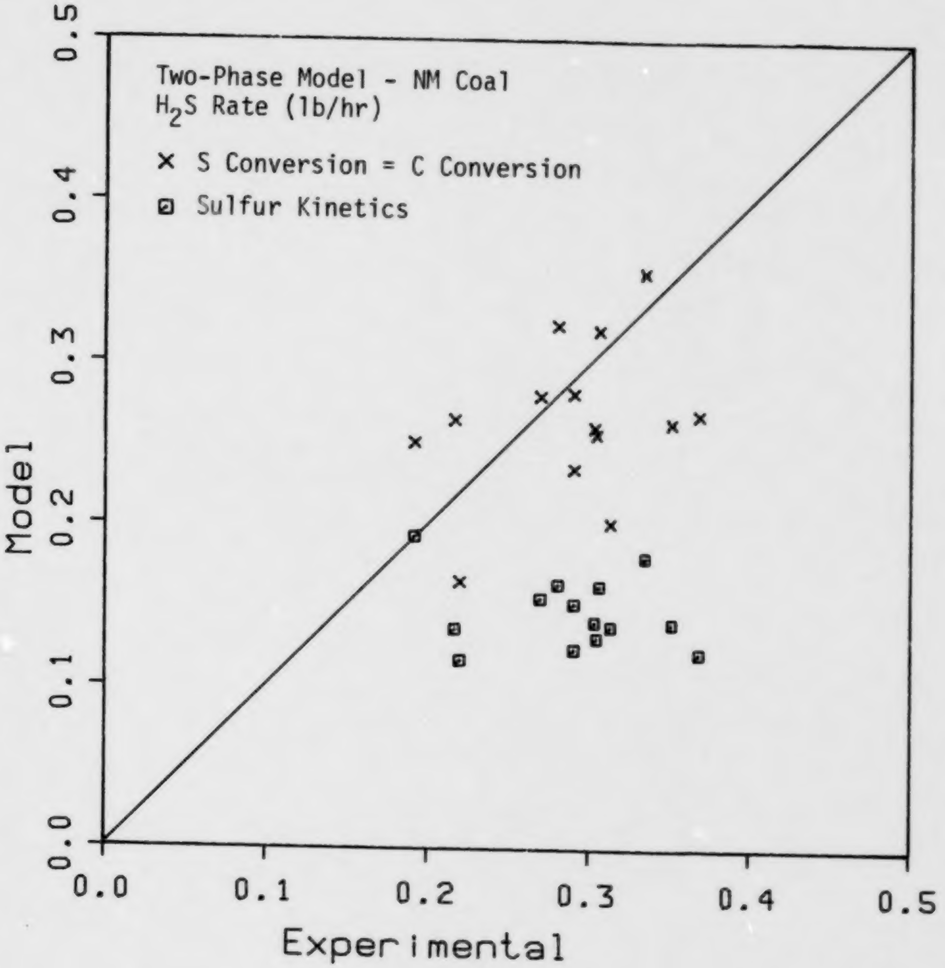

FIGURE 48

PREDICTED VS. EXPERIMENTAL HYDROGEN SULFIDE PRODUCTION RATE FOR NM COAL, TWO-PHASE MODEL

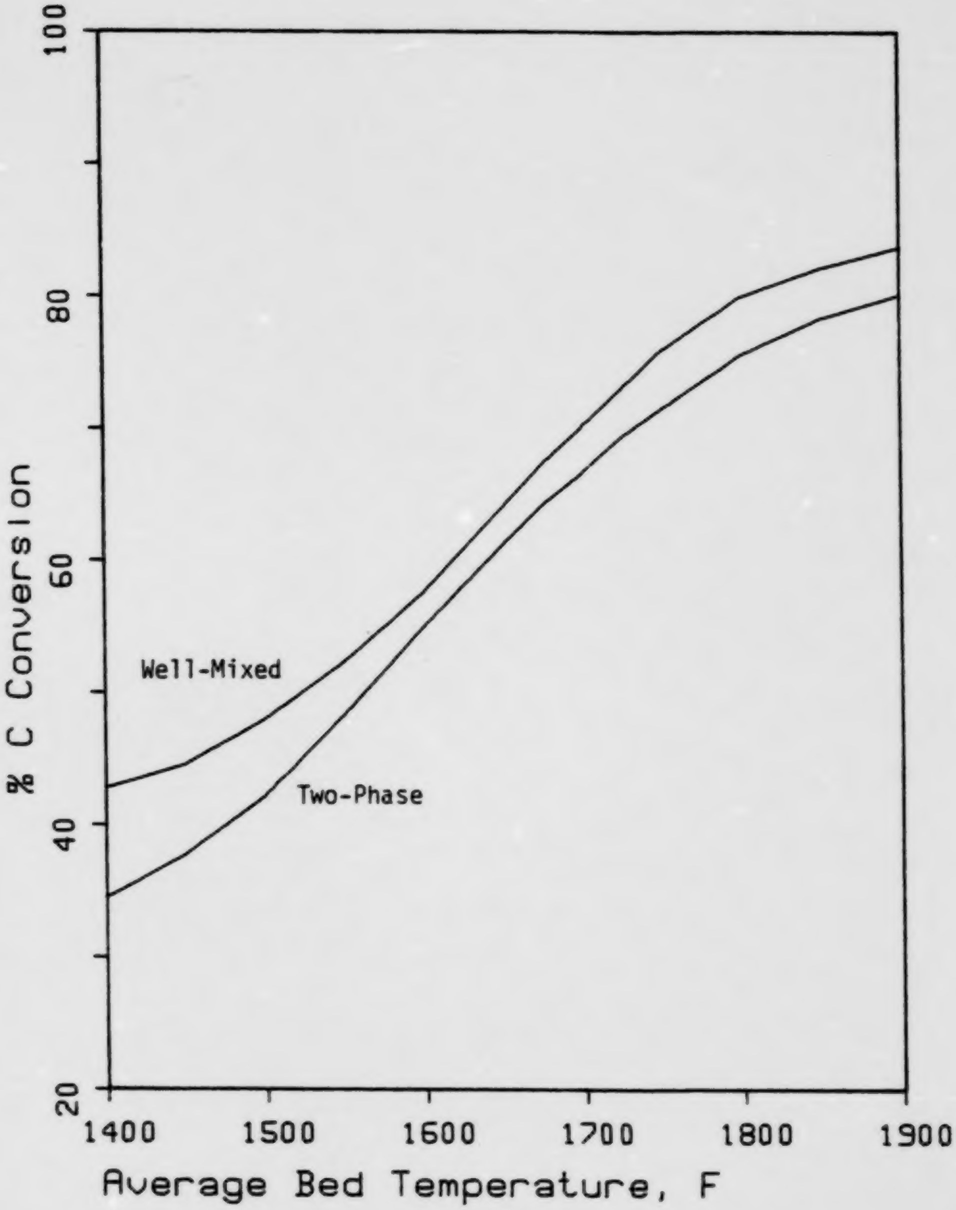

FIGURE 49

PREDICTED EFFECT OF AVERAGE BED TEMPERATURE
ON CARBON CONVERSION

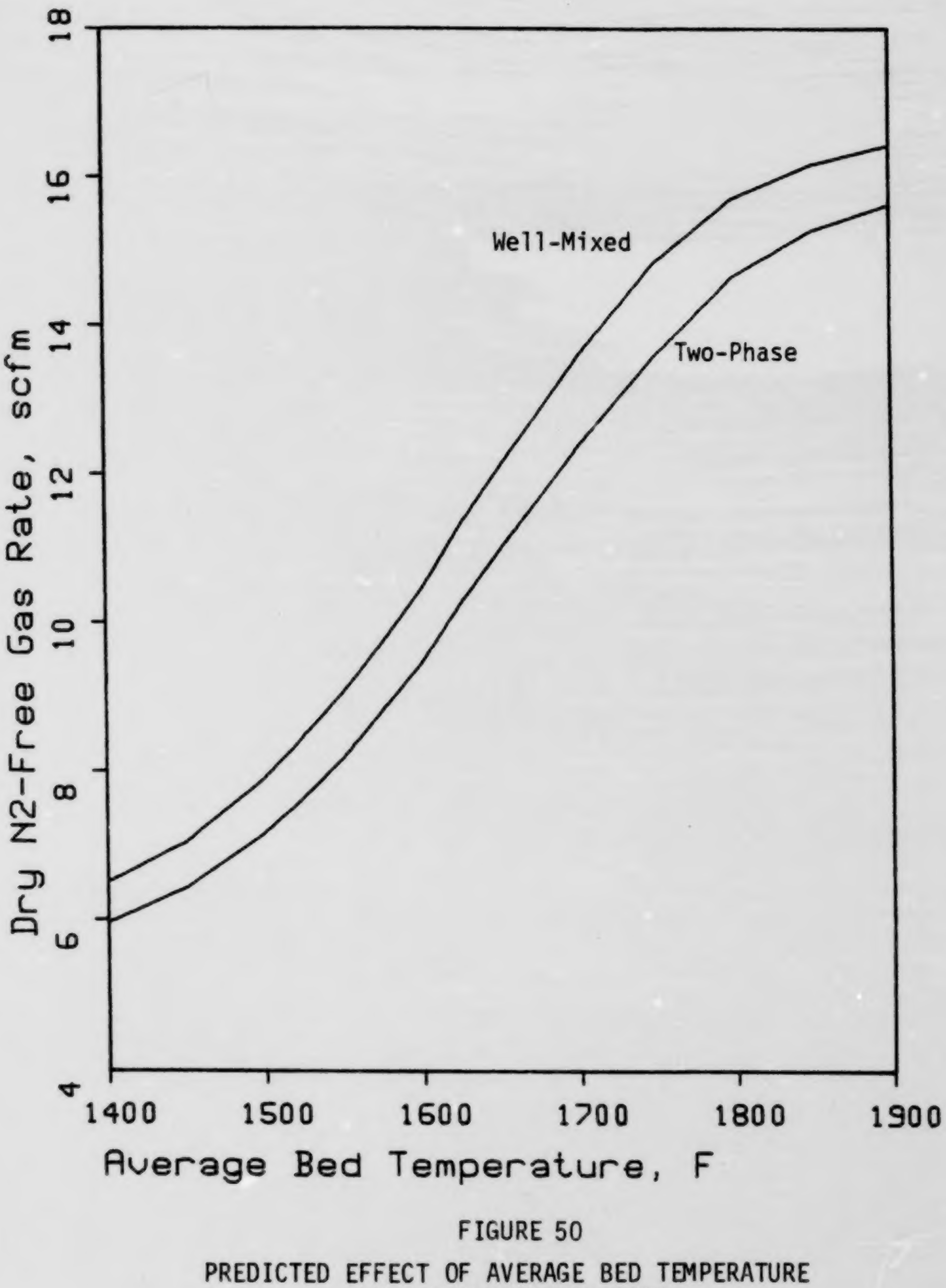

FIGURE 50

PREDICTED EFFECT OF AVERAGE BED TEMPERATURE ON GAS PRODUCTION RATE steep increases in the range 1500-1750^{o}F. Above 1750^{o}F the increases slow due to depletion of carbon in the fluidized bed. The increases in carbon conversion and gas production are a result of increases in both the devolatilization product yields and the reaction rates in the fluidized bed. Both models show the same trends of conversion and gas production versus temperature. For the chosen conditions, the well-mixed model predicts higher conversions and gas production rates than the two-phase model, with the differences being roughly the same for the entire temperature range. The effects of temperature as determined from experimental results are similar to those predicted by the models.

Steam/Carbon Feed Ratio

Run GO-84 was used to provide the base operating conditions for determining the effect of the molar H_2O/C feed ratio. The steam feed rate was varied to give a H_2O/C feed ratio of 0.5 to 2.0. The nitrogen feed rate was simultaneously adjusted to maintain a inlet gas velocity of 0.9-1.1 ft/s. All other operating variables were held constant. The predicted effects on carbon conversion and gas production are shown in Figures 51 and 52. Both conversion and gas production increase with increasing H_2O/C ratio. This is most likely due to enhancement of the steam-carbon gasification reaction rate. Increasing the steam rate also increases the extent of the water gas shift reaction toward the gases H_2 and CO. Comparison of the two models shows similar trends. The well-mixed model predicted lower conversions than the two-phase model for the conditions examined, and predicted a lesser dependence of the gas production rate on the H_2O/C ratio than was found for the well-mixed model.

Solid-Phase Space Time

The solid-phase space time is defined as the solids holdup in the reactor divided by the coal feed rate. The effect of the solid-phase space time on reactor performance was determined by varying the bed height while fixing all other operating variables at constant values. The operating conditions of run GO-69B were chosen as the base conditions. Figures 53 and 54 show the predicted effects of the solid-phase space time on carbon conversion and gas production. Both increase with increasing space time. The effects are greatest at low

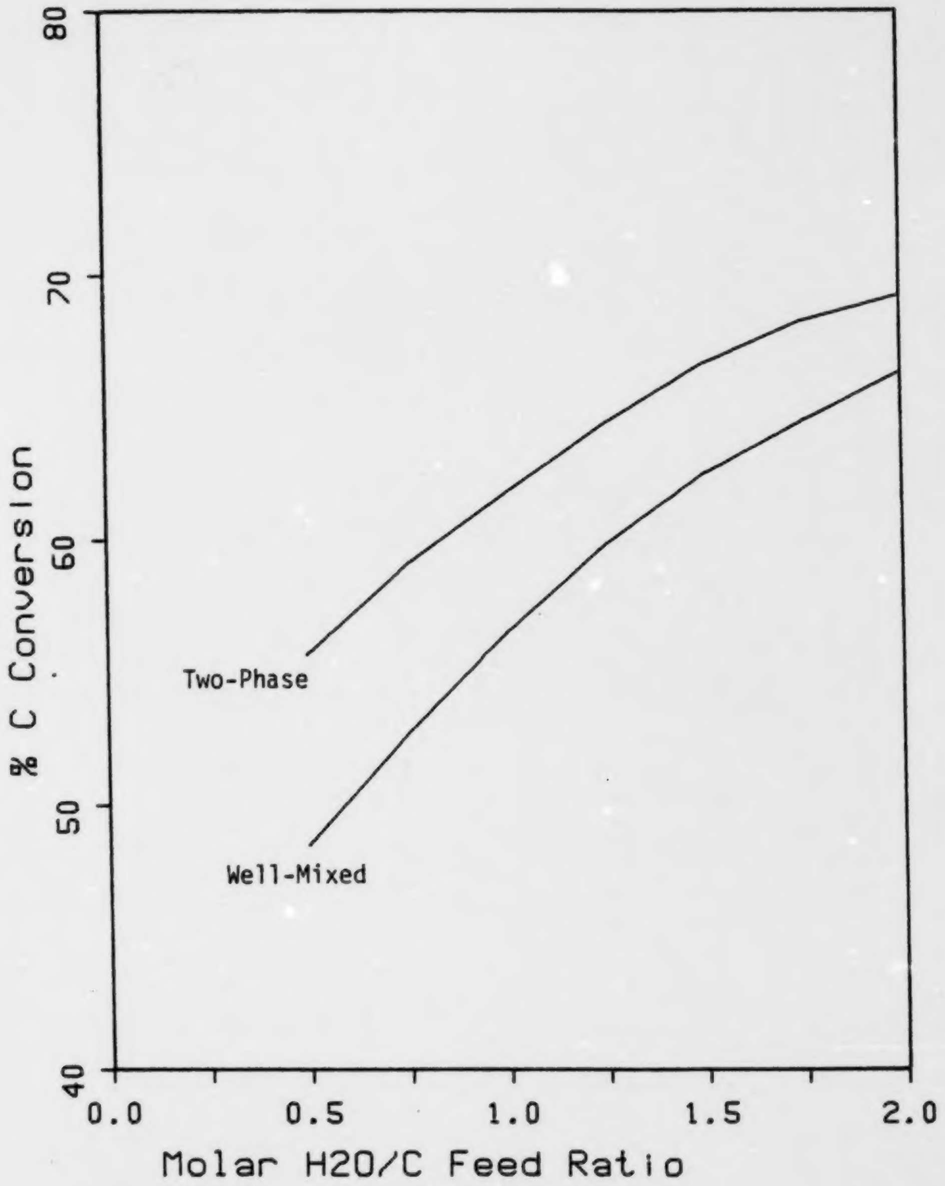

FIGURE 51

PREDICTED EFFECT OF STEAM-TO-CARBON FEED RATIO ON CARBON CONVERSION

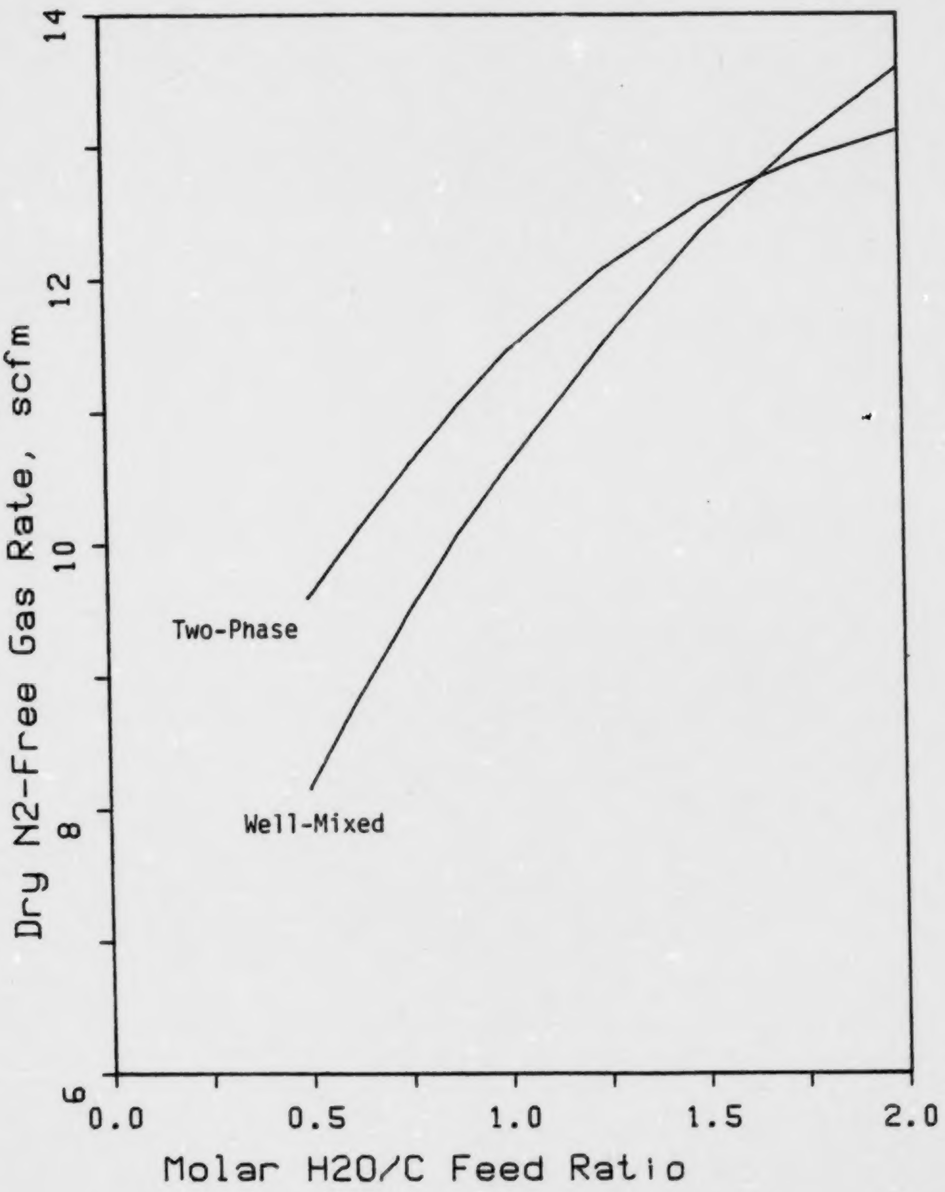

FIGURE 52

PREDICTED EFFECT OF STEAM-TO-CARBON FEED RATIO ON GAS PRODUCTION RATE

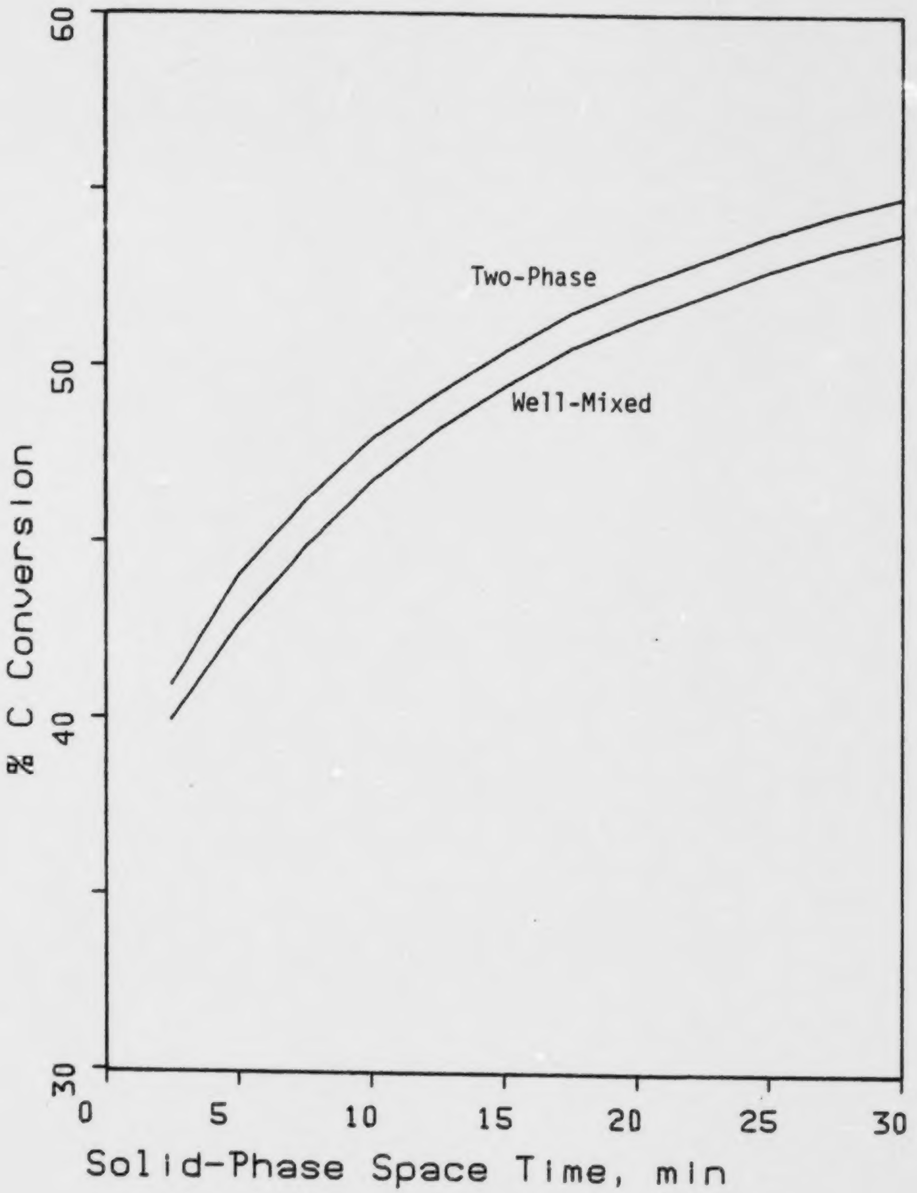

FIGURE 53

PREDICTED EFFECT OF SOLID-PHASE SPACE TIME
ON CARBON CONVERSION

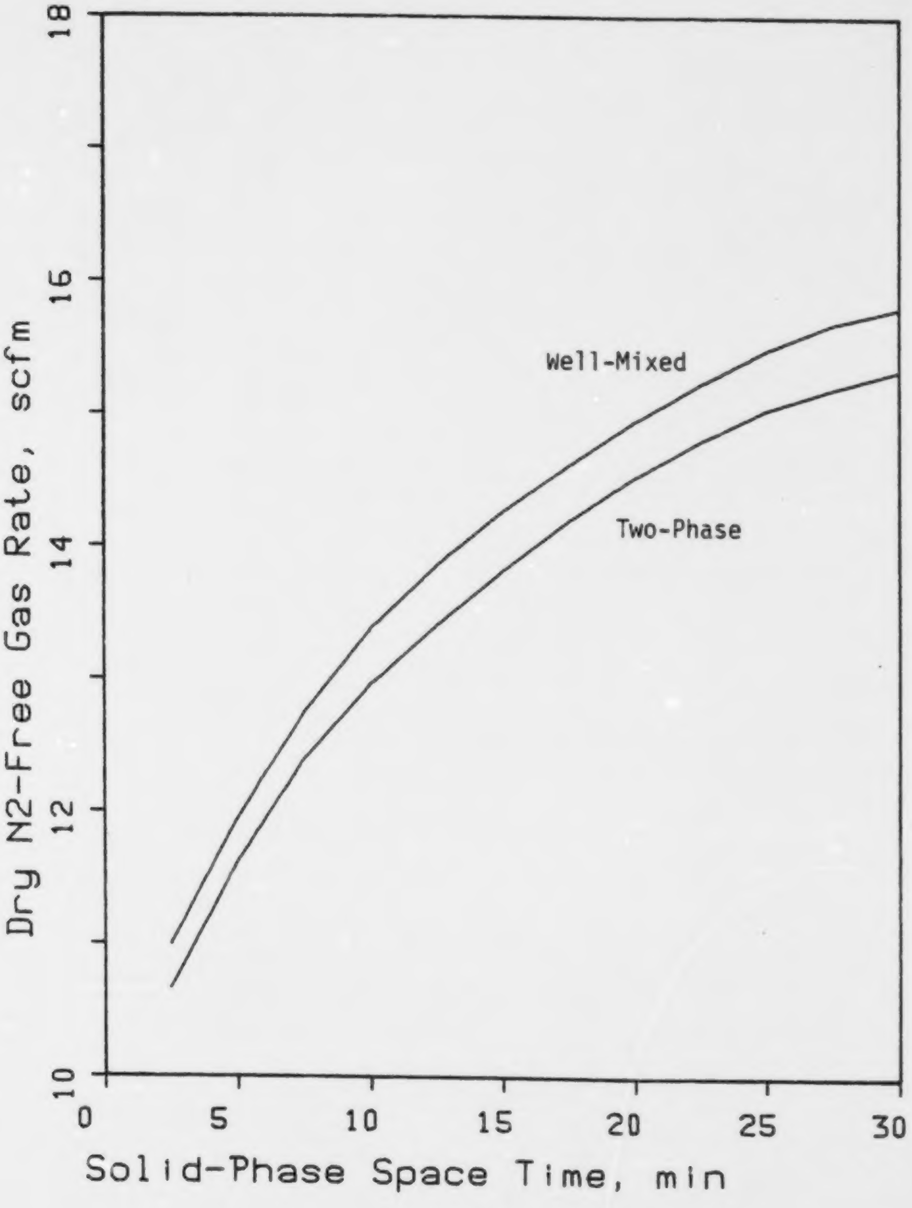

FIGURE 54

PREDICTED EFFECT OF SOLID-PHASE SPACE TIME
ON GAS PRODUCTION RATE

space times, and the effects lessen with increasing space time. The individual gas species all showed similar monotonic increases with increasing space time. The two models yielded nearly identical curves of predicted conversion and gas production versus the solid-phase space time.

Feed Particle Size Distribution

The two-phase model takes the feed particle size distribution into account, whereas the well-mixed model does not require knowledge of the size distribution. The two-phase model was run for several feed size distributions to determine the effect on reactor performance predictions. All operating conditions were held constant except the feed size distribution, and were taken from the data of gasifier run GO-78. The results are given in Table 22. Distribution 3 is the experimentally determined distribution; the others are hypothetical distributions. The results show that the feed size distribution has a dramatic effect on the elutriation and char rates, but only a small effect on carbon conversion and gas production. As would be expected, the small particle size distribution lead to a high elutriation rate, while there was no elutriation with the large particle size distribution. Carbon conversion and gas production were similar for the three larger size distributions, and slightly lower for the small size distribution. The gas compositions, on a dry basis, show a decrease in the CO/CO_2 ratio with increasing particle size. The hydrogen content in the dry gas increased with increasing particle size.

COMPUTATION

The well-mixed and two-phase reactor models are both implemented by Fortran computer programs. A description of the components of the well-mixed program and complete source code listings are given in Appendix A, and a description of the programming that comprises the two-phase model is given in Appendix B along with complete source code listings.

TABLE 22
EFFECT OF FEED PARTICLE SIZE DISTRIBUTION ON MODEL PREDICTIONS

	Feed Particle Size Distribution			
	1	2	3	4
Sieve Analysis *				
12	0.00	0.00	0.17	25.00
20	0.00	5.00	29.75	27.50
30	0.00	17.50	18.46	25.00
40	5.00	27.50	16.08	12.50
60	10.00	27.50	18.76	5.00
80	17.50	17.50	8.82	2.50
100	30.00	5.00	3.94	1.50
200	20.00	0.00	2.82	1.00
325	10.00	0.00	0.41	0.00
pan	7.50	0.00	0.79	0.00
Avg Dia, microns	177	470	691	1084
Model Predictions				
C Conversion, %	53.2	58.3	56.5	57.9
Dry Gas Rate, scfm	14.37	15.36	15.10	15.57
Dry Gas Comp, mole %				
CO	17.09	15.42	13.29	11.56
CO_2	17.82	19.76	21.74	23.05
H_2	26.00	27.05	27.10	28.28
CH_4	6.18	6.97	6.55	6.72
Elutriation Rate, lb/hr	20.37	3.77	0.97	0.00
Spent Char Rate, lb/hr	0.00	13.50	16.42	16.91
Char Avg Dia, microns	--	250	387	801
Elut Avg Dia, microns	73	192	82	--

* sieve analyses in wt % retained on sieve

All modeling work was performed using three computers housed in the NCSU Department of Chemical Engineering. The three computers used were all products of the Digital Equipment Corporation. Initial work was done with a PDP-11/34. The 11/34 had sufficient capabilities to run the well-mixed model, but was slow when running the two-phase model. Both models were also run on a PDP-11/23, which was slower than the 11/34. However, it had the advantage of few users, thus it could be devoted to modeling programs. The computing problem was greatly eased with the addition of a VAX-750 to the departmental computing facility. The VAX had sufficient capabilities to run the two-phase reactor model program in reasonable time spans. Table 23 lists typical CPU times required by each program on the three different computers.

TABLE 23
CPU REQUIREMENTS OF MODELING PROGRAMS

	CPU Time, min	
	Well-Mixed	Two-Phase
PDP-11/23	< 1	100
PDP-11/34	< 1	30
VAX-750	< 0.5	6

APPLICABILITY OF MODELS

The gasifier models are currently limited to the simulation of a top feeding fluidized-bed reactor. In commercial use, it is probable that fluidized bed reactors will use a deep-bed coal feed system. The major modification required to model this reactor design deals with the coal devolatilization products. The current models assume no interaction of the volatiles with the fluidized bed. Interaction should not be neglected with a deep-bed coal feed system.

The models were developed for simulation of an oxygen-blown reactor. However, an air-blown system can be easily handled by proportioning the air feed rate between the oxygen and nitrogen feed rates. If recycle of the product gas is employed, revisions of the programs would be required. Recycle would require an additional iterative loop in each program.

Both the well-mixed model and the two-phase model did a good job of correlating data from the NCSU pilot-scale gasification reactor. In theory, both could be applied to any other top-feeding gasifier. Due to its simplicity, the ability of the well-mixed model to model other systems is uncertain. The two-phase model is probably more applicable to differing systems, as its consideration of the bed hydrodynamics should make it a more general model. The capability of the two-phase model to consider such effects as jetting and elutriation add to its generality.

Before either model can be applied to a gasification system, information on the coal to be gasified is required. Standard coal characterization data, such as proximate and ultimate analyses, density, and size distribution, are needed. In addition, values of the model parameters -- char reactivity, shift reactivity, combustion product coefficient, and abrasion constant -- are required to run the model. Ideally, the parameters should be evaluated from plant data. In many cases plant data may be unavailable. In this case, a bench-scale reactor might be capable of yielding the same information. It is also possible that if sufficient data for the parameters values for various coals are obtained, parameter correlations as functions of easily measured coal properties could be developed. The parameters values are difficult to determine, but once obtained they are applicable to any set of gasification conditions. The parameters are properties of the coal, and are independent of the processing conditions.

SUMMARY AND CONCLUSIONS

A devolatilized Kentucky bituminous coal, a New Mexico subbituminous coal, a North Carolina peat, and a Texas lignite were gasified with steam and oxygen in a pilot-scale fluidized-bed reactor. The reactor was operated at pressures of 570-840 kPa (80-120 psia), molar steam-to-carbon feed ratios of 0.6 to 1.9, and average bed temperatures of 795-1010^{o}C (1460-1850^{o}F). The coal feed rate ranged from 14 to 33 kg/hr (30-73 lb/hr). The experimental results were used to provide a basis for the evaluation of mathematical models of the gasification reactor.

A simple three-stage model of the gasifier was the first step in reactor modeling studies. The model assumes instantaneous devolatilization of coal at the top of the fluidized-bed, instantaneous combustion of carbon at the bottom of the bed, and steam/carbon gasification and water gas shift reaction in a single perfectly mixed isothermal stage.

A two-phase bubbling-bed gasifier model was also developed. The fluidized bed is assumed to consist of an incipiently fluidized emulsion phase and a solids-free bubble phase. The solids are assumed to be well-mixed as in the simple model, but plug flow of the gases is assumed. Model options allow for consideration of a jetting region at the gas inlet of the bed and elutriation of fines.

The gasification reactions in each model were described by the Johnson kinetics. Carbon combustion was assumed to go to instantaneous completion in the well-mixed model, while oxidation kinetics were incorporated into the two-phase model. For the water gas shift reaction, the common assumption of shift equilibrium was used, as were shift kinetics.

Sulfur gas production rates were estimated by assuming equality of the sulfur and carbon conversions, with all converted sulfur forming H_2S. Yergey-Vestal kinetic rate expressions for H_2S formation were also incorporated into the two-phase model. For either case of H_2S formation, the rate of COS formation was determined by assuming equilibrium of the sulfur shift reaction ($H_2S + CO_2 = COS + H_2O$).

Devolatilization calculations must be included in the model for gasification of a raw coal feedstock. For the New Mexico coal, the equilibrium fractional weight loss was estimated from a temperature-dependent correlation. Tar was estimated to be 34% by weight of the total devolatilization products, and the devolatilized gases were assumed to have the following composition: 28% H_2, 19% CO, 16% CO_2, 37% CH_4, 0.2% H_2S, and 0.014% COS.

The models were applied to the gasification of the devolatilized Kentucky bituminous coal and the New Mexico subbituminous coal. Parameter optimizations were performed with each model for each feedstock. The main difference in the optimal values was in the char reactivity parameter, for which that of the New Mexico coal was roughly an order of magnitude greater than that for the Kentucky char. Using the optimal parameter values, the models were run for all experimental runs. The resulting model predictions and experimental results showed reasonably good agreement in all cases.

Evaluation of a sum of squared errors function indicated that the well-mixed model yielded slightly better correlations of run data than did the two-phase model. This result may be due in part to the fact that a more exhaustive parameter search was carried out to fit the simpler model to the experimental data; better correlations could be achieved with the two-phase model if a more refined optimization procedure were to be employed. However, the improvements in goodness-of-fit that might be obtained thereby would probably not justify the extensive computation time that would be required to obtain them.

The assumption of water gas shift reaction equilibrium was examined by comparing experimental results with model predictions obtained by assuming equilibrium and by use of shift kinetics. Assumption of equilibrium led to severe overprediction of K_{wg}, while significant improvements in the results were obtained when shift kinetics were taken into account. The results indicated that for the conditions of the NCSU gasifier, the shift reaction should not be assumed to proceed to equilibrium.

An elutriation prediction method was included in the two-phase model. Model predictions and experimental measurements showed fair agreement. The elutriation correlation is sensitive to the particle density and size distribution. The feed measurements and modeling assumptions concerning the density and size distribution are most likely a primary source of the discrepancy between predictions and experimental measurements. Model predictions for carbon conversion, gas production rate, and gas composition are essentially unaffected by consideration of elutriation. To obtain quantitative measure of the effect of elutriation consideration, the sum of squared errors function was evaluated for each case. The results -- 0.060 with elutriation and 0.062 without elutriation -- show the small improvement obtained by adding the complexity of elutriation to the model.

The two-phase model can also consider a jetting region at the gas inlet of the reactor. The model was run with the jetting region neglected and with the jetting region included. For the New Mexico coal runs, there were few differences between model predictions for the two cases. Evaluation of the sum of squared errors function (values of 0.058 and 0.060) confirmed that there is little difference in the correlations obtained for the two cases. For a hypothetical case featuring a shallow bed and high gas feed rates, consideration of a jetting region was shown to be more important.

Predictions of sulfur gas formation were compared for the cases of sulfur reaction kinetics and the assumption of equal sulfur and carbon conversions. The method of sulfur kinetics consistently underpredicted the H_2S and COS production rates, while the assumption of equal conversions yielded reasonably good correlations. The poor correlations for sulfur kinetics are probably related to the assumptions concerning the sulfur form distribution in the coal. The kinetics are highly dependent on the sulfur distribution, so that small errors could lead to the consistent underprediction seen in this research.

The effect of differing temperature profiles on reactor performance was also examined. For a fixed set of reactor inputs and a fixed average bed temperature, model results showed significant differences with changing temperature profile. High temperatures in the bottom of the reactor coupled with low temperatures in the top of the bed led to predictions of higher carbon conversions, gas production rates, and CO/CO_2 ratios. The model was run for the New Mexico coal runs using the experimentally measured temperature profiles, as well as with the average bed temperature calculated for each run. For these runs, there were no major differences in the predicted conversions and gas rates. Evaluation of the sum of squared errors function indicated that a slightly better correlation is obtained using the average temperature (0.047 for the average temperature case and 0.060 for the case of experimental temperature profiles).

The model was used in parametric studies to observe the effect of reactor operating parameters. Carbon conversion and gas production both increase with increasing temperature and steam/carbon feed ratio. This is expected, as increasing temperature increases the extent of devolatilization as well as the rates of reaction in the fluidized bed. Increases in the steam/carbon feed ratio enhance the steam-carbon gasification rate, and increase the extent of the water gas shift reaction toward the gases CO_2 and H_2. Increases in the solid-phase space time, when achieved by increasing the bed height, also yield increases in carbon conversion and gas production rates. The feed particle size distribution was shown to have a dramatic effect on the elutriation and char rates, but only a small effect on carbon conversion and gas production. Both models showed the same qualitative trends with variations in the reactor operating variables.

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APPENDIX A: WELL-MIXED MODEL COMPUTER PROGRAM

The well-mixed reactor model program is written in FORTRAN. The components of the model are listed below with brief descriptions of their main functions.

DSSMOD - Main program. Coordinates overall calculational procedure. Handles input and output operations.

DEVOL - calculates devolatilization product yields.

PRGUES - gives initial estimate of carbon conversion and gas production rates.

BEDRXN - coordinates iterative fluidized bed calculations.

RATES - calculates reaction rates.

STOICH - performs species mass balances.

SHIFT - adjusts gas flow rates to achieve equilibrium of the water-gas shift reaction.

COS - adjusts gas flow rates to achieve equilibrium of the sulfur shift reaction ($COS + H_2O = H_2S + CO_2$).

CONV - provides new rate estimates for use in iterative calculations.

The required input for the program is as follows:

TITLE - comment string. maximum of 32 characters allowed.

PSIG - reactor pressure, psig

TFAHR - reactor temperature, °F

WSOLID - solids holdup in reactor, lb

BHT - height of fluidized bed, in

BDIA - diameter of fluidized bed, in

WCHAR - coal feed rate, lb/hr

WH2O - steam feed rate, lb/hr

WO2 - oxygen feed rate, lb/hr

WN2 - nitrogen feed rate, lb/hr

WH2 - hydrogen feed rate, lb/hr

WPURN2 - purge nitrogen feed rate, lb/hr

XUCH(i) - ultimate analysis of feed coal, wt percents.
1=C, 2=H, 3=O, 4=N, 5=S, 6=ash.

XPROX(i) - proximate analysis of feed coal, wt percents.
1=fixed C, 2=volatile matter, 3=moisture, 4=ash.

TEMPO - pretreatment temperature of feed coal (if any), ^{o}F

FO - char reactivity factor

EXTENT - CO/CO_2 combustion production distribution coefficient

FWG - shift reactivity factor

VOID - estimated fractional bed voidage

The following three input parameters are model options:

IK - sulfur gas shift reaction equilibrium option.
IK=0 indicates use of equilibrium equation of Purdy,
IK=1 indicates use of data of Kohl and Riesenfeld.

WGOPT - water gas shift reaction option.
WGOPT=0 for assumption of equilibrium,
WGOPT=1 for use of shift reaction kinetics.

DOPT - devolatilization option.
DOPT=0 indicates no devolatilization (for a char feed),
DOPT=1 for consideration of devolatilization.

The following input parameters are not essential for running the program, as they are merely experimental results included in the output for easy comparison with the model predictions.

XCH - weight % carbon in the spent char

GASEX - dry make gas flow rate, scfm

H2OCEX - fractional steam conversion

XTTLEX - fractional carbon conversion

YASHEX - weight % ash in the spent char

CRREX - spent char removal rate, lb/hr

HVEX - heating value of sweet gas, Btu/scf

YEX(i) - product gas composition, mole percents.
1=O_2, 2=CO, 3=H_2, 4=CH_4, 5=CO_2,
6=N_2, 7=H_2S, 8=COS, and 9=H_2O.

Source code listings for the program are given in the following pages.

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```
C...  THIS IS THE MAIN PROGRAM FOR A STEADY-STATE, WELL-MIXED COAL
C...  GASIFICATION MODEL.  DEVOLATILIZATION IS OPTIONAL, AND
C...  EQUIL OF   H2S+CO2=COS+H2O  IS ASSUMED. SHIFT EQUIL OR
C...  SHIFT KINETICS MAY BE USED, AS DICTATED BY WGOPT.
c...
c...  variables directory
c...  bdia     bed diameter, inches
c...  bht      bed height, inches
c...  combus   amount of carbon combusted in reactor, lbmole/min
c...  crr      predicted char removal rate, lb/hr
c...  crrex    experimental char removal rate, lb/hr
c...  dopt     devolatilization option (0=none, 1=devol.)
c...  extent   an empirical parameter which determines how the char
c...           combustion products are distributed between co and co2.
c...           0.5=only co formed; 1.0=only co2 formed.
c...  f(i)     flowrate of gas components into the reactor, lbmole/min
c...  fd(i)    component flowrates from devolatilization, lbmole/min
c...  feedc    initial feed rate of carbon, (lb c)/hr
c...  fo       adjustable parameter which reflects the char reactivity
c...  fwg      shift reaction reactivity factor
c...  g(i)     generation rate of each component in the bed, lbmole/min
c...  gas      dry gas flow rate, scfm
c...  gasex    experimental dry gas flow rate, scfm
c...  gasexw   experimental wet gas flow rate, lbmoles/hr
c...  h2ocex   experimental fractional conversion of inlet styeam
c...  i        component index: 1=o2; 2=co; 3=h2; 4=ch4; 5=co2; 6=n2;
c...           7=h2s; 8=cos; 9=h2o; 10=carbon.
c...  icard    set to non-zero value if estimated rates are provided
c...  keq      equilibrium constant for shift reaction
c...  kex      experimental k ratio for shift rxn
c...  km       model k ratio for shift rxn
c...  patm     reactor pressure in atmoshperes absolute
c...  prd(i)   the product rate of each component, lbmole/min
c...  prdttl   total product gas flowrate, lbmole/min
c...  psig     reactor pressure in psig
c...  qex(i)   experimental effluent flows, lb/hr
c...  qm(i)    model effluent flows, lb/hr
c...  spec(i)  gas component names: O2,cO,h2,ch4,cO2,n2,h2s,cos,h2o
c...  t        reactor temperature, rankine
c...  tar      tar formation rate, lb/hr
c...  tempo    highest temperature the carbon has experienced, rankine.
c...           used to adjust the char reactivity.
c...  tfahr    reactor temperature in fahrenheit
c...  title(k) descriptive title input by user. less than 32 characters
c...  void     estimated bed voidage fraction
c...  wchar    mass of char (including ash) entering reactor, lb/hr
c...  wgopt    water-gas shift rxn option:  0=equil, 1=kinetics
c...  wh2      hydrogen entering reactor, lb/hr
c...  wh2o     steam entering reactor, lb/hr
c...  wn2      nitrogen entering reactor, lb/hr
c...  wo2      oxygen entering reactor, lb/hr
c...  wpurn2   purge nitrogen, lb/hr
c...  wsolid   mass of all solids in reaction zone, lb
c...  x(i)     ultimate analysis of char entering gas. zone (wt %)
c...  xch      ultimate analysis of carbon in the product char, wt %
c...  xcomb    the fractional carbon conversion due to combustion
c...  xdevol   the fractional carbon conversion due to devolatilization
c...  xgasn    fractional carbon conversion due to gasification
c...  xmw(i)   molecular weights of gas components
c...  xprox    prox analysis of feed coal (1=fc, 2=vm, 3=moist, 4=ash)
c...  xtot     avg carbon conversion of the bed solids, wt. fraction
c...  xttl     overall fractional carbon conversion
c...  xttlex   experimental overall carbon conversion
```

```
c...  xuch(j)  the ultimate analysis of the solid in the bed, wt %
c...           1 = c; 2 = h; 3 = o; 4 = n; 5 = s; 6 = ash
c...  y(i)     the mole percent of gas in the bed on a solid-free basis
c...  yash     weight fraction ash in the product char
c...  yashex   experimental wt fraction ash in the product char
c...  yex(i)   experimental mole percent of gas
c...
      dimension title(8),xuch(6),f(10),prd(10),g(10),y(9),dx(4),yex(8),
     *  spec(9),xmw(9),fd(9),xprox(4),x(6),qex(9),qm(9),hv(3),qmd(9),
     *  qmb(9)
      common/block1/tempo,fo,xdevol,xcomb
      common/block3/void,fws,bht
      common/block4/combus
      common/block5/k1,ik
      integer wsopt,dopt
      real keq,kex,km,k1ex,k1
      data spec/'O2 ','CO ','H2 ','CH4','CO2','N2 ','H2S','COS','H2O'/
      data xmw/31.99,28.01,2.02,16.04,44.01,28.01,34.08,60.07,18.02/
      data hv/1.218e5,1.230e5,3.381e5/
      open(unit=3,name='lp.lst',type='new')
 1999 read(1,2000,end=1120)(title(i),i=1,8)
 2000 format(8a4)
      read(1,2001)psig,tfahr,wsolid,bht,bdia
 2001 format(8f10.0)
 2004 format(3f10.0,e10.2,f10.0)
      read(1,2001)wchar,wh2o,wo2,wn2,wh2,wpurn2
      read(1,2001)(xuch(i),i=1,6)
      read(1,2004)tempo,fo,extent,fws,void
      read(1,2001)xch,gasex,h2ocex,xttlex,yashex,crrex,hvex
      read(1,2001)(yex(i),i=2,9)
      read(1,2001)(xprox(i),i=1,4)
      read(1,2005)ik
      read(1,2005)wsopt
      read(1,2005)dopt
 2005 format(i1)
      patm=(psig+14.696)/14.696
      t=tfahr+459.67
      tempo=tempo+459.67
c...  subroutine devol is called to compute the devolatilization state
c...  products:
      feed=wchar
      feedc=wchar*xuch(1)/100.
      do 400 i=1,6
      x(i)=xuch(i)
  400 continue
      do 401 i=1,9
      fd(i)=0.0
  401 continue
      tar=0.0
      xdevol=0.0
      if(dopt.eq.0) go to 402
      call devol(t,wchar,xuch,xprox,fd,tar)
c...  call coss to adjust the devol sulfur gases to be in equilibrium
      call coss(fd,t)
      xdevol=(fd(2)+fd(4)+fd(5)+fd(8))*12.01*60.0/feedc
c...  compute inlet flows to fluidized bed:
  402 f(10)=(wchar*xuch(1))/(12.01*60.*100.)
      f(1)=wo2/(32.0*60.)
      f(2)=0.0
      f(3)=wh2/(2.016*60.)
      f(4)=0.0
      f(5)=0.0
      f(6)=wn2/(28.02*60.)
      f(7)=0.0
      f(8)=0.0
      f(9)=wh2o/(18.01*60.)
c...  the following computes the combustion reactions.
      f(5)=f(5)+(2.-1./extent)*f(1)
      f(2)=f(2)+(2./extent-2.)*f(1)
      combus=f(1)/extent
      xcomb=combus*12.01*60.0/feedc
      f(10)=f(10)-combus
      f(1)=0.0
      if(icard.ne.0)go to 2003
      xtot=0.20
c...  prgues is called to provide first guesses for the
c...  product composition
      call prgues(f,xtot,prd)
c...  bedrxn is called to compute the steady state flows
 2003 continue
      call bedrxn(t,patm,f,wsolid,prd,xuch,xtot,g,wsopt)
c...  loop 513 sums the lbmoles of gas produced
      prd(6)=prd(6)+wpurn2/(28.02*60.0)
      prdttl=0.0
      do 513 i=1,9
      prd(i)=prd(i)+fd(i)
      prdttl=prdttl+prd(i)
  513 continue
c...  loop 514 computes the product mole fractions
      do 514 i=1,9
      y(i)=(prd(i)/prdttl)*100.
  514 continue
      gas=prdttl*359.0*(1.-y(9)/100.)
      xttl=(prd(2)+prd(4)+prd(5)+prd(8))*12.01*60.0/feedc
      xgasn=xttl-xdevol-xcomb
c...  calculate experimental and model effluent flows in lb/hr
      gasexw=gasex/((1-yex(9)/100)*359)*60.0
      do 900i=2,9
      aex(i)=gasexw*(yex(i)/100)*xmw(i)
      amd(i)=fd(i)*60.0*xmw(i)
      am(i)=prd(i)*60.0*xmw(i)
      amb(i)=am(i)-amd(i)
  900 continue
c...  calculate sweet gas heating value (btu/scf)
      hvm=(prd(2)*hv(1)+prd(3)*hv(2)+prd(4)*hv(3))/(359.*(prd(2)+prd(3)
     1    +prd(4)+prd(6)-wpurn2/(60.*28.02)))
c...  calculate water-gas 'k' values
      keq=exp(8395.2/t - 4.29)
      kex=yex(3)*yex(5)/(yex(9)*yex(2))
      km =y(3)*y(5)/(y(9)*y(2))
c...  calculate experimental sulfur shift rxn 'k' value
      k1ex=yex(7)*yex(5)/(yex(8)*yex(9))
c...  calculate sulfur gas concentrations on dry ppm basis
      yh2sm=y(7)/(1-y(9)/100.)*1.0e4
      ycosm=yh2sm*y(8)/y(7)
      yh2se=yex(7)/(1-yex(9)/100.)*1.0e4
      ycose=yh2se*yex(8)/yex(7)
c...  print results:
      write(3,1000)
 1000 format(1h1,/////)
      write(3,1001)
 1001 format(T34,'WELL-MIXED COAL GASIFICATION MODEL RESULTS')
      write(3,1002)(title(i),i=1,8)
 1002 format(/t41,8a4)
      write(3,1006)
 1006 format(//t20,'REACTOR SPECIFICATIONS',T63,'FEEDRATES (LB/HR)')
```

```
      write(3,1007)psig,feed
 1007 format(/T20,'BED PRESSURE(PSIG)',T42,F7.2,T63,'INLET COAL',
     1T81,F10.2)
      write(3,1008)tfahr,wh2o
 1008 format(T20,'BED TEMPERATURE(F)',T42,F7.2,T63,'STEAM',T81,F10.2)
      write(3,1009)wsolid,wo2
 1009 format(T20,'SOLIDS HOLDUP(LB)',T42,F7.2,T63,'OXYGEN',T81,F10.2)
      write(3,1010)bht,wn2
 1010 format(T20,'BED HEIGHT(IN)',T42,F7.2,T63,'NITROGEN',T81,F10.2)
      write(3,1011)bdia,wh2
 1011 format(T20,'BED DIAMETER(IN)',T42,F7.2,T63,'HYDROGEN',T81,F10.2)
      write(3,1032)void,wpurn2
 1032 format(T20,'BED VOIDAGE',T42,F7.2,T63,'PURGE N2',T81,F10.2)
      write(3,1012)
 1012 format(//T20,'MODEL PARAMETERS',T63,'FEED COAL ANALYSIS (WT %)')
      write(3,1013)fo,x(1)
 1013 format(/T20,'CHAR REACTIVITY',T42,F7.4,T63,'CARBON',T81,F10.2)
      write(3,1014) extent,x(2)
 1014 format(T20,'COMBUSTION EXTENT',T42,F7.4,T63,'HYDROGEN',T81,F10.2)
      if(wsopt.eq.1) write(3,1015)fws
 1015 format(T20,'SHIFT REACTIVITY',T39,1PE10.3)
      if(wsopt.eq.0) write(3,1021)
 1021 format(T20,'SHIFT EQUILIBRIUM')
      write(3,1019)x(3)
 1019 format('+',T63,'OXYGEN',T81,F10.2)
      write(3,1016)x(4)
 1016 format(T63,'NITROGEN',T81,F10.2)
      write(3,1017)x(5)
 1017 format(T63,'SULFUR',T81,F10.2)
      write(3,1018)x(6)
 1018 format(T63,'ASH',T81,F10.2,/)
      write(3,1020)
 1020 format(/T60,'MODEL',4X,'EXPERIMENTAL')
      write(3,1022)gas,gasex
 1022 format(/T28,'DRY GAS FLOW RATE (SCFM)',T60,F5.2,7X,F5.2)
      write(3,1026)
 1026 format(/T28,'CARBON CONVERSION')
      if(dopt.eq.1) write(3,1027)xdevol
 1027 format(T30,'DEVOLATILIZATION',T60,F5.3)
      write(3,1028)xcomb
 1028 format(T30,'COMBUSTION',T60,F5.3)
      write(3,1030)xgasn
 1030 format(T30,'GASIFICATION',T60,F5.3)
      write(3,1034)xttl,xttlex
 1034 format(T30,'TOTAL',T60,F5.3,7X,F5.3)
      write(3,1036)hvm,hvex
 1036 format(/T28,'SWEET GAS HEATING',/T30,'VALUE (BTU/SCF)',
     1   t60,f5.1,7x,f5.1)
      write(3,1040)
 1040 format(//T39,'GAS COMPOSITION (MOLE PERCENT)')
      write(3,1041)
 1041 format(/T49,'MODEL',4X,'EXPERIMENTAL',/)
      write(3,1042)y(2),yex(2)
 1042 format(T39,'CO',T49,F5.2,7X,F5.2)
      write(3,1044)y(3),yex(3)
 1044 format(T39,'H2',T49,F5.2,7X,F5.2)
      write(3,1046)y(4),yex(4)
 1046 format(T39,'CH4',T49,F5.2,7X,F5.2)
      write(3,1048)y(5),yex(5)
 1048 format(T39,'CO2',T49,F5.2,7X,F5.2)
      write(3,1050)y(6),yex(6)
 1050 format(T39,'N2',T49,F5.2,7X,F5.2)
      write(3,1052)y(7),yex(7)
```

```fortran
1052 format(T39,'H2S',T49,F5.2,7X,F5.2)
     write(3,1054)y(8),yex(8)
1054 format(T39,'COS',T49,F5.2,7X,F5.2)
     write(3,1056)y(9),yex(9)
1056 format(T39,'H2O',t49,f5.2,7x,f5.2)
     write(3,1000)
     write(3,1001)
     write(3,1002)(title(i),i=1,8)
     write(3,1100)
1100 format(///T41,'EFFLUENT FLOW RATES (LB/HR)')
     write(3,1102)
1102 format(/T51,'MODEL',12X,'EXPERIMENTAL',//T44,'DEVOL',
    *   3X,'GASN',4X,'TOTAL',/)
     do 1104i=2,9
     write(3,1106)spec(i),amd(i),amb(i),am(i),aex(i)
1104 continue
1106 format(T33,A3,7X,F5.2,F8.2,F8.2,7X,F5.2)
     write(3,1107)tar,tar
1107 format(T33,'TAR',7X,F5.2,4X,'0.00',F8.2)
     write(3,1108)
1108 format(////T41,'SHIFT REACTION K RATIO:')
     write(3,1110)
1110 format(/T41,'MODEL',4X,'EXPERIMENTAL',4X,'EQUILIBRIUM')
     write(3,1112)km,kex,keq
1112 format(/T41,F5.3,7X,F5.3,10X,F5.3)
     write(3,1114)
1114 format(////T41,'SULFUR GAS SHIFT RXN K RATIO:')
     write(3,1116)k1,k1ex
1116 format(/T41,'MODEL',4X,'EXPERIMENTAL'//,T41,F5.2,7X,F5.2)
     write(3,1118)
1118 format(//T41,'SULFUR GASES (PPM,DRY):',//,T47,'MODEL',4X,
    1 'EXPERIMENTAL')
     write(3,1119)yh2sm,yh2se,ycosm,ycose
1119 format(/T41,'H2S  ',F6.1,6X,F6.1,/T41,'COS  ',f6.1,6x,f6.1)
     write(3,1000)
     go to 1999
1120 stop
     end
```

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```
      SUBROUTINE DEVOL(T,WCHAR,XUCH,XPROX,FD,TAR)
C**********************************************************************
C     AVGMW =  AVERAGE MOL WT OF DEVOLATILIZED GASES
C     CHAR  =  SOLID FLOW RATE AFTER DEVOLATILIZATION
C     DAFWL =  DRY-ASH-FREE WEIGHT LOSS (WT FRACTION)
C     FD(I) =  FLOW RATE OF DEVOL GASES, LBMOLES/MIN
C     FDTOT =  TOTAL FLOW RATE OF DEVOLALITILZED GASES
C     FTAR  =  FRACTION OF WDEVOL THAT IS TAR
C     T     =  TEMPERATURE, RANKINE
C     TK    =  TEMPERATURE, KELVIN
C     TAR   =  AMOUNT OF TAR PRODUCED, LBS/HR
C     WCHAR =  FEED RATE OF COAL, LBS/HR
C     WDEVOL=  MASS OF COAL DEVOLALITIZED(excluding moisture), LBS/HR
C     WLOSS =  MASS OF COAL DEVOLATILIZED(including moisture), LBS/HR
C     X     =  INTERMEDIATE USED TO CALCULATE XUCH (WT PERCENT)
C     XPROX =  PROXIMATE ANALYSIS (WT PERCENTS)
C     XTAR  =  TAR ULTIMATE ANALYSIS (WT PERCENTS)
C     XUCH  =  ULTIMATE ANALYSIS (WT PERCENTS)
C     XMW   =  MOL WEIGHTS OF GASES, LBS/LBMOLE
C     YD    =  MOLE FRACTIONS OF DEVOL GASES
C***********************************************************************
      dimension xuch(6),xprox(4),fd(9),yd(9),xmw(9),xtar(6)
      data xmw/31.99,28.01,2.02,16.04,44.01,28.01,34.08,60.07,18.02/
      data yd/0.0,0.194,0.279,0.372,0.155,0.0,0.002,0.00014,0.0/
      data xtar/85.0,5.0,9.0,0.5,0.5,0.0/
      ftar=0.34
      tk=(5./9.)*t
C-----CALCULATE FLOW RATES OF DEVOLALITIZATION PRODUCTS
      dafwl=1.05-7.15e-3*tk+1.61e-5*tk*tk-1.37e-8*tk**3+4.04e-12*tk**4
      wdevol=wchar*dafwl*(100.-xprox(3)-xprox(4))/100.
      avgmw=0.0
      do 100 i=2,8
      avgmw=avgmw+xmw(i)*yd(i)
 100  continue
      tar=ftar*wdevol
      fdtot=(wdevol-tar)/(avgmw*60.0)
      do 150 i=1,8
      fd(i)=fdtot*yd(i)
 150  continue
      fd(9)=xprox(3)*wchar/(100.*60.*xmw(9))
C-----CALCULATE NEW COAL FLOW RATE AND COMPOSITION
C-----(MAKE SURE ALL WT FRACTIONS NON-NEGATIVE)
      char=wchar*(1.0-xprox(3)/100.0)-wdevol
      x=(xuch(2)*wchar-xtar(2)*tar-2.02*60.*
     *     (fd(3)+2*fd(4)+fd(7)+fd(9))*100.)/char
      if(x.ge.0.0) go to 200
      adjust=xuch(2)*wchar/(xuch(2)*wchar-x*char)
      tar=tar*adjust
      fd(3)=fd(3)*adjust
      fd(4)=fd(4)*adjust
      fd(7)=fd(7)*adjust
      fd(9)=fd(9)*adjust
      wloss=tar
      do 195 i=1,9
 195  wloss=wloss+fd(i)*xmw(i)*60.0
      char=wchar-wloss
 200  x=(xuch(3)*wchar-xtar(3)*tar-16.00*60.0*
     *     (fd(2)+2*fd(5)+fd(8)+fd(9))*100.)/char
      if(x.ge.0.0) go to 210
      adjust=xuch(3)*wchar/(xuch(3)*wchar-x*char)
      tar=tar*adjust
      fd(2)=fd(2)*adjust
      fd(5)=fd(5)*adjust
      fd(8)=fd(8)*adjust
      fd(9)=fd(9)*adjust
      wloss=tar
      do 205 i=1,9
205   wloss=wloss+fd(i)*xmw(i)*60.0
      char=wchar-wloss
210   x=(xuch(5)*wchar-xtar(5)*tar-32.06*60.0*
     *     (fd(7)+fd(8))*100.)/char
      if(x.ge.0.0) go to 220
      adjust=xuch(5)*wchar/(xuch(5)*wchar-x*char)
      tar=tar*adjust
      fd(7)=fd(7)*adjust
      fd(8)=fd(8)*adjust
      wloss=tar
      do 215 i=1,9
215   wloss=wloss+fd(i)*xmw(i)*60.0
      char=wchar-wloss
220   xuch(5)=(xuch(5)*wchar-xtar(5)*tar-32.06*60.0*
     *    (fd(7)+fd(8))*100.)/char
      xuch(2)=(xuch(2)*wchar-xtar(2)*tar-2.02*60.0*
     *     (fd(3)+2*fd(4)+fd(7)+fd(9))*100.)/char
      xuch(3)=(xuch(3)*wchar-xtar(3)*tar-16.0*60.0*
     *     (fd(2)+2*fd(5)+fd(8)+fd(9))*100.)/char
      xuch(4)=(xuch(4)*wchar-xtar(4)*tar)/char
      xuch(6)=xuch(6)*wchar/char
      xuch(1)=100.0-(xuch(2)+xuch(3)+xuch(4)+xuch(5)+xuch(6))
      wchar=char
c
      return
      end
```

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```
      subroutine coss(prd,btem)
c...
c...  COSS ADJUSTS THE GAS COMPOSITION TO ACCOUNT FOR THE ASSUMED
c...  EQUILIBRIUM OF THE RXN   COS + H2O = H2S + CO2.  THE EQUIL.
c...  CONSTANT EQN CAN BE THAT DETERMINED BY PURDY (8-80), OR THAT
c...  TAKEN FROM DATA PRESENTED BY KOHL AND RIESENFELD(DATA OF TERRES
c...  AND WESEMANN).
c...
c...  variables directory:
c...  btem     avg bed temp, degrees rankine
c...  ik       parameter which determines which equilibrium constant is
c...           used:   ik=0 - purdy,   ik=1 - terres and wesemann.
c...  k1       equil constant for the rxn  cos + h2o = h2s + co2
c...  prd(i)   the product rate of each component, lbmoles/min,
c...           5=co2; 7=h2s; 8=cos; 9=h2o.
c...  root     quadratic eqn solution, =lbmoles of cos produced,...
c...  t        avg bed temp, degrees kelvin
c...  term1    intermediate used in soln of quadratic eqn,
c...           similarly for term2 and term3.
c...
      dimension prd(11)
      common/block5/k1,ik
      real k1
      if(prd(7).le.0.0.and.prd(8).le.0.0) return
      t=btem*5/9
      if(ik.eq.1) go to 3
      k1=exp(3.293+3864.34/t-0.49*alog(t)-4.143e-4*t
     1  +5.596e-7*t*t-1.558e-10*t**3)
      go to 4
    3 k1=exp(-1.352+7881.61/btem)
    4 term1=k1*(prd(8)+prd(9))+prd(5)+prd(7)
      term2=k1-1.0
      term3=sqrt(term1**2-4*term2*(k1*prd(8)*prd(9)-prd(5)*prd(7)))
      root1=(-term1+term3)/(2*term2)
      root2=(-term1-term3)/(2*term2)
      root=root1
      if(root1.gt.prd(7).or.(prd(8)+root1).lt.0.0) go to 5
      go to 6
    5 root=root2
      if(root2.gt.prd(7).or.(prd(8)+root2).lt.0.0) return
    6 prd(5)=prd(5)-root
      prd(7)=prd(7)-root
      prd(8)=prd(8)+root
      prd(9)=prd(9)+root
      return
      end
      subroutine prgues(f,xest,prd)
c...
c...  INITIAL ESTIMATES ARE MADE OF THE OUTLET GAS COMPOSITION USING
c...  AN ASSUMED CARBON CONVERSION, XEST, AND ASSUMING ONLY THE STEAM
c...  CARBON REACTION IS IMPORTANT.  CH4 IS TAKEN TO BE A SMALL
c...  FRACTION OF THE OTHER REACTIVE GASES.
c...
c...  variables directory:
c...  f(i)      flowrate of i into the gasification zone, lbmole/min
c...  prd(i)    flowrate of i from the gasification zone, lbmole/min
c...  xest      initial guess for the carbon conversion in the zone
c...
      real f(10),prd(10)
c...  this checks to insure that sufficient steam is present to
c...  reach the initially estimated carbon conversion.
   17 continue
      if(f(9)-(f(10)*xest))19,19,22
   19 xest=xest/2.
      write(3,20)
   20 format('  initial estimate for carbon conversion was too
     1 large and was reduced by one-half')
      go to 17
   22 continue
c...  this estimates product rates assuming c + h2o = co + h2o
      prd(1)=f(1)
      prd(2)=f(2)+xest*f(10)
      prd(3)=f(3)+xest*f(10)
      prd(4)=0.01*(f(2)+f(3)+f(5)+f(9))
      prd(5)=f(5)
      prd(6)=f(6)
      prd(7)=f(7)
      prd(8)=f(8)
      prd(9)=f(9)-xest*f(10)
      prd(10)=f(10)*(1.-xest)
      return
      end
      subroutine bedrxn(t,p,f,xmass,prd,xuch,xtot,g,wgopt)
c...
c...  GIVEN TEMP, PRESSURE, FEEDRATES, SOLID HOLDUP, COAL ANALYSIS
c...  AND ESTIMATED VALUES FOR PRODUCT RATES AND CARBON CONVERSION,
c...  BEDRXN CALCULATES STEADY STATE PRODUCT RATES
c...
c...  variables directory:
c...  dx(1)    wt fraction of carbon consumed per min by c+h2o = co+h2
c...  dx(2)    wt fraction of carbon consumed per min by c + 2h2 = ch4
c...  dx(3)    wt fraction of c consumed per min by 2c+h2+h2o = co+ch4
c...  dx(4)    shift rxn rate, lbmoles/min
c...  dxc(i)   intermediate values for the rates dx(i)
c...  f(i)     flowrate of gas components into the reactor, lbmole/min
c...  g(i)     generation rate of each component in the bed, lbmole/min
c...  i        component index: 1=o2; 2=co; 3=h2; 4=ch4; 5=co2; 6=n2;
c...           7=h2s; 8=cos; 9=h2o; 10=carbon.
c...  nc       a convergence flag.  1=converged;  2=unconverged
c...  p        reactor pressure, atm
c...  prd(i)   the product rate of each component, lbmole/min
c...  prdtot   total gas production from the bed, lbmole/min
c...  t        reactor temperature, rankine
c...  wgopt    shift rxn option:  0=equil,  1=kinetics
c...  xbase    base carbon conversion, fractional
c...  xmass    solids holdup in the bed, lbs
c...  xtot     average carbon conversion of the coal, wt. fraction,
c...           based on solids present after devol and combustion
c...  xtotn    intermediate value for xtot
c...  xuch(j)  the ultimate analysis of the solid in the bed, wt %
c...           1 = c; 2 = h; 3 = o; 4 = n; 5 = s; 6 = ash
c...  y(i)     gas mole fractions in the bed
c...
c...  the units used in calculation are lbs, lb-moles, degrees rankine,
c...  atm, cubic feet, and minutes.
      dimension f(10),g(10),y(9),prd(10),xuch(6),dx(4),dxc(4)
      integer wgopt
      nc=0
      jj=0
      dx(1)=0.0100
      dx(2)=-0.0005
      dx(3)=0.0025
      dx(4)=0.0020
      if(wgopt.eq.0) dx(4)=0.0
      go to 2002
 2001 call stoich(t,dx,f,xuch,xtot,xmass,g,prd,xbase)
 2002 continue
c...  loop 103 is the overall iteration loop for convergence.
c...  a maximum of 300 iterations is specified
      do 103 k=1,300
c...  loop 105 computes the total product gas rate
      prdtot=0.0
      do 105 i=1,9
      prdtot=prdtot+prd(i)
  105 continue
c...  loop 106 calculates the gas mole fractions
      do 106 i=1,9
      y(i)=prd(i)/prdtot
  106 continue
      if(wgopt.eq.1) go to 109
c...  subroutine shift is called to give a gas composition which
c...  satisfies water-gas shift equilibrium.
      call shift(t,y,sh2)
      y(2)=y(2)-sh2
      y(9)=y(9)-sh2
      y(3)=y(3)+sh2
      y(5)=y(5)+sh2
      do 107 i=1,9
      prd(i)=y(i)*prdtot
  107 continue
c...  subroutine rates is called to compute the solid-gas reaction
c...  rates, and provide new values for dx(j)
  109 call rates(p,t,xtot,y,dxc,xbase)
      if(wgopt.eq.0) dx(4)=0.0
c...  subroutine conv is called to iterate for the correct dx(j)
      call conv(dx,dxc,4,nc)
      go to (6,5),nc
    5 continue
c...  call subroutine stoich to get material balances for zone
      call stoich(t,dx,f,xuch,xtot,xmass,g,prd,xbase)
c...  subroutine coss is called to adjust the gas flow rates,
c...  assuming equilibrium for the rxn   cos+h2o=co2+h2s
      call coss(prd,t)
      term=-g(10)/f(10)
  202 xtotn=0.9*xtot+0.1*term
      if(1.-xtotn)203,203,204
  203 term=term/2.
      go to 202
  204 xtot=xtotn
  103 continue
      jj=jj+1
      write(3,108)
  108 format('  caution: convergence criteria of 0.05 percent was
     1 not satisfied for every reaction rate')
      if (jj.eq.2) go to 4030
  6   continue
      if (nc.ne.1) go to 2001
 4030 return
      end
      subroutine stoich(t,dx,f,xuch,xtot,xmass,g,prd,xbase)
c...
c...  STOICH ACCEPTS THE REACTION RATES FROM SUBROUTINE RATES,
c...  GASIFICATION ZONE FEEDRATES, INLET COAL COMPOSITION, OVERALL
c...  CARBON CONVERSION, AND SOLIDS HOLDUP.  IT YIELDS THE GENERATION
c...  RATE OF EACH COMPONENT AND THE GASIFICATION ZONE PRODUCT RATES.
c...
c...  variables directory:
c...  dx(1)    wt fraction of carbon consumed per min by c+h2o = co+h2
c...  dx(2)    wt fraction of carbon consumed per min by c + 2h2 = ch4
c...  dx(3)    wt fraction of c consumed per min by 2c+h2+h2o = co+ch4
c...  dx(4)    shift reaction rate, lbmoles/min
c...  f(i)     flowrate of i into the gasification zone, lbmole/min
c...  g(i)     generation rate of each component in the bed, lbmole/min
c...  prd(i)   flowrate of i from the gasification zone, lbmole/min
c...  rxmolc   molar rate of carbon entering the gasification zone, lbmoles
c...  term4    used to shorten the expressions for g(i)
c...  xbase    fractional base carbon conversion
c...  xmass    the weight of all solids, including ash, in the zone, lb
c...  xtot     the average conversion of the carbon in the bed
c...  xuch(j)  the ultimate analysis of the solid in the bed, wt %
c...           1 = c; 2 = h; 3 = o; 4 = n; 5 = s; 6 = ash
c...  yash     the weight fraction of ash in the zone solids
c...  ycar     the weight fraction of carbon in the zone solids
c...
      dimension dx(4),f(10),xuch(6),g(10),prd(10)
      common/block4/combus
c...  this calculates the molar carbon holdup.  the bed ash content
c...  is calculated first using the value of xtot and
c...  the inlet char ash content.
      yash=xuch(6)/((1.-xtot)*(100.-xuch(6))+xuch(6))
      ycar=(1.-yash)*(xuch(1)/(xuch(1)+xuch(2)+xuch(3)+xuch(4)+xuch(5)))
      rxmolc=(xmass*ycar)/(12.01*(1.0-xbase))
c...  generation rates are computed from johnson kinetics
c...  and assuming that the ratio of s,o,n,&h to carbon in the char is
c...  constant. s to h2s; o to co; n to n2; h to h2
      term4=12.01*(combus+rxmolc*(dx(1)+dx(2)+dx(3)))/xuch(1)
      g(1)=0.0
      g(2)=rxmolc*(dx(1)+0.5*dx(3))+(term4*xuch(3))/16.0
      g(3)=rxmolc*(dx(1)-2.*dx(2)-0.5*dx(3))+((term4*xuch(2))/2.016)-
     1 (term4*xuch(5))/32.06
      g(4)=rxmolc*(dx(2)+0.5*dx(3))
      g(5)=0.0
      g(6)=(term4*xuch(4))/28.01
      g(7)=(term4*xuch(5))/32.06
      g(8)=0.0
      g(9)=rxmolc*(-dx(1)-0.5*dx(3))
      g(10)=-rxmolc*(dx(1)+dx(2)+dx(3))-(term4*xuch(3))/16.0
c...  product rates are calculated from the generation rates
      do 51 i=1,10
c...  a check is made for negative rates.  if found, the product
c...  rate is set to 0.1* the prior value
      if(f(i)+g(i))49,50,50
   49 prd(i)=0.1*prd(i)
      go to 51
   50 prd(i)=f(i)+g(i)
   51 continue
c...  adjust rates to reflect degree of shift reaction
      call shift(t,prd,sh2)
      if(abs(sh2).lt.abs(dx(4))) dx(4)=sh2
      g(2)=g(2)-dx(4)
      g(9)=g(9)-dx(4)
      g(3)=g(3)+dx(4)
      g(5)=g(5)+dx(4)
c...  product rates are re-calculated from the generation rates
c...  and a check is made for negative rates.
      do 61 i=1,10
      if(f(i)+g(i))59,60,60
  59  prd(i)=0.1*prd(i)
      go to 61
  60  prd(i)=f(i)+g(i)
  61  continue
      return
      end
      subroutine shift(btem,y,sh2)
c...
c...  SHIFT DETERMINES THE EXTENT OF THE WATER GAS SHIFT
c...  REACTION REQUIRED TO ACHIEVE EQUILIBRIUM.
c...
c...  variables directory:
c...  btem      bed temperature, rankine
c...  eq4       equilibrium constant for the shift reaction
c...  root1     one of the two roots for sh2
c...  root2     one of the two roots for sh2
c...  sh2       denotes the degree of the shift reaction toward h2
c...  term1     used to solve the quadriatic equation for sh2
c...  term2     used to solve the quadriatic equation for sh2
c...  y(i)      gas mole fractions
c...
      real y(9)
      eq4=exp(8395.2/btem-4.29)
      term1=(y(5)+y(3)+(y(2)+y(9))*eq4)/(2.*(1.-eq4))
      term2=(y(5)*y(3)-eq4*y(2)*y(9))/(1.-eq4)
      root1=-term1+sqrt(term1**2-term2)
      root2=-term1-sqrt(term1**2-term2)
c...  this selects the root of smaller absolute magnitude
c...  as the meaningful root
      if(abs(root1)-abs(root2))3,4,5
    3 sh2=root1
      go to 6
    4 sh2=0.0
      go to 6
    5 sh2=root2
    6 continue
      end
      subroutine rates(p,btem,xtot,y,dx,xbase)
c...
c...  RATES ACCEPTS PRESSURE, TEMPERATURE, AVERAGE CARBON CONVERSION,
c...  GAS COMPOSITION AND PROVIDES THE RATES OF THE THREE REACTIONS
c...  USED BY JOHNSON TO CORRELATE SLOW-RATE CHAR GASIFICATION REACTIONS.
c...
c...  variables directory:
c...  alpha     intermediate used in calculating char reactivity
c...  bht       bed height, inches
c...  btem      bed temperature, rankine
c...  cwg       constant used in shift rxn rate eqn
c...  dx(1)     wt fraction of carbon consumed per min by c+h2o = co+h2
c...  dx(2)     wt fraction of carbon consumed per min by c + 2h2 = ch4
c...  dx(3)     wt fraction of c consumed per min by 2c+h2+h2o = co+ch4
c...  dx(4)     rate of the shift rxn, lbmoles/min
c...  eqi       equilibrium constant for reaction i
c...  eqii      equilibrium constant for reaction ii
c...  eqiii     equilibrium constant for reaction iii
c...  eqiv      equilibrium constant for thhe shift reaction
c...  fo        char reactivity parameter
c...  f1        intermediate used in calculating char reactivity
c...  fwg       shift reaction reactivity factor
c...  p         bed pressure, atm
c...  ppres(i)  partial pressure of each component, atm
c...  rki       rate of reaction i as defined by johnson.
c...  rkii      rate of reaction ii as defined by johnson.
c...  rkiii     rate of reaction iii as defined by johnson.
c...  tempo     a parameter which represents the highest temperature
c...            the carbon has experienced, rankine.
c...  term3     intermediate term used for calculational efficiency
c...  v         volume of fluidized bed, cm**3
c...  void      estimated bed voidage fraction
c...  xbase     fractional base carbon conversion
c...  xtot      the average conversion of the carbon in the bed
c...  y(i)      gas mole fractions on a solid-free basis
c...
      dimension y(9),ppres(9),dx(4)
      common/block1/tempo,fo,xdevol,xcomb
      common/block3/void,fwg,bht
      eqi=exp(-29010.6/btem+17.09)
      eqii=exp(17744.4/btem-12.23)
      eqiii=eqi*eqii
      eqiv=exp(8395.2/btem-4.29)
c...  tempo represents the highest temperature to which the char has
c...  been exposed.  if the zone temperature is greater than tempo,
c...  then tempo is set equal to the zone temperature.
      if(btem-tempo)101,100,100
  100 tempo=btem
  101 continue
c...  loop 11 calculates the partial pressures.
      do 11 i=1,9
      ppres(i)=y(i)*p
   11 continue
c...  alpha and f1 are reactivity parameters for the char.
      alpha=52.7*ppres(3)/(1.0+54.3*ppres(3))+0.521*sqrt(ppres(3))*
     1    ppres(9)/(1.0+0.707*ppres(9)+0.5*sqrt(ppres(3))*ppres(9))
      f1=fo*exp(8467./tempo)
c...  calculate johnson kinetic parameters
      rki=(ppres(9)*(exp(9.0201-31705./btem))*(ppres(9)-((ppres(2)*
     1   ppres(3))/eqi)))/((ppres(9)+((exp(-22.2160+44787./btem))*(1.0
     2   +16.35*ppres(3)+43.5*ppres(2))))**2)
```

```
      rkii=((exp(2.6741-33076./btem))*(ppres(3)**2-ppres(4)/eqii))/
     1   (1.+ppres(3)*(exp(-10.4520+19976./btem)))
c...  a check is required to prevent division by zero if neither
c...  hydrogen or methane are present, or if no water is present.
c...  check bypasses rate eqn iii if neither are present.
      if((ppres(3)+ppres(4)).gt.1.0e-10)go to 21
      rkiii=0.0
      go to 22
   21 continue
      rkiii=(ppres(3)**1.5*exp(12.4463-44544./btem)*(ppres(3)*ppres(9)-
     1      ppres(2)*ppres(4)/eqiii))/(ppres(3)+exp(-6.6696+15198./btem)
     2      *(ppres(3)**1.5+0.85*ppres(2)*ppres(3)+18.62*ppres(4)))**2
   22 continue
      cwg=16652.0
      v=463.296*bht
      xbase=(xtot*(1.0-xdevol-xcomb)+xcomb)/(1.0-xdevol)
      term3=fl*(1.-xbase)**0.6667*exp(-alpha*xbase**2)
      dx(1)=rki*term3
      dx(2)=rkii*term3
      dx(3)=rkiii*term3
      if(y(9).le.0.0)go to 30
      dx(4)=v*(1.-void)*fwg*cwg*exp(-25147.4/btem)*p*
     1  (y(2)-y(3)*y(5)/(y(9)*eqiv))
      return
   30 dx(4)=0.0
      return
      end
      SUBROUTINE CONV(X,XC,N,NC)
C...
C...  CONV SUPPLIES NEW RATE ESTIMATES TO BE USED IN THE
C...  ITERATIVE CONVERGENCE SCHEME.
C...  MODIFIED SUCCESSIVE SUBSTITUTION AND DOMINANT
C...  EIGEN VALUE METHODS ARE USED.  DOMINANT EIGEN VALUE METHOD
C..   IS USED FOR ACCELERATION WHENEVER EIGEN VALUE STABILITY IS
C...  ACHIEVED.  OTHERWISE SUBSTITUTION IS USED.
C...
C...  VARIABLES DIRECTORY
C...  EV        EIGEN VALUE
C...  EVL       EIGEN VALUE FROM PRIOR ITERATION
C...  N         NUMBER OF VARIABLES BEING SIMULTANEOUSLY CONVERGED
C...  NC        CONVERGENCE FLAG.  1=CONVERGED, 2=NONCONVERGED.
C...  NORM      THE NORM OF THE X(I) VECTOR
C...  NORML     NORM CALCULATED FROM PRIOR ITERATION
C...  OLDX(I)   X(I) FROM PRIOR ITERATION
C...  OLDXC(I)  XC(I) FROM PRIOR ITERATION
C...  X(I)      VALUES USED IN F(X)
C...  XC(I)     VALUES CALCULATED FROM XC=F(X)
C...  XD        VALUE CALCULATED BY DE METHOD
C...  XT        VALUE CALCULATED BY SUBSTITUTION METHOD
C...
      DIMENSION X(N),XC(N),OLDX(10),OLDXC(10)
      REAL NORM,NORML
      KOUNT=KOUNT+1
C...  CHECK FOR CONVERGENCE
      DO 10 I=1,N
      IF(X(I).EQ.0.0.AND.XC(I).EQ.0.0) GO TO 10
      IF((ABS(X(I)-XC(I))/(ABS(X(I))+ABS(XC(I)))).GT.0.0005) GO TO 20
   10 CONTINUE
C...  IF CONVERGED:
      DO 15 I=1,N
   15 X(I)=XC(I)
      NC=1
      KOUNT=0
      RETURN
C...  IF NOT CONVERGED:
   20 NC=2
C...  CALCULATE NORM AND EIGEN VALUE
   40 SUM=0.0
      DO 50 I=1,N
   50 SUM=SUM + (X(I)-OLDX(I))**2
      NORM=SQRT(SUM)
      IF(NORML.EQ.0.0) GO TO 55
      EV=NORM/NORML
      DEV=ABS((EV-EVL)/EV)
   55 CONTINUE
C...  CHECK TO SEE IF DE METHOD CAN BE USED
      IF(NIT.LT.5.OR.DEV.GT.0.01) GO TO 100
C...  DE METHOD:
      NIT=0
      DO 60 I=1,N
      XD=OLDX(I) + 0.7*(X(I)-OLDX(I))/(1-EV)
      OLDX(I)=X(I)
   60 X(I)=XD
      GO TO 200
C...  SUBSTITUTION METHOD:
  100 NIT=NIT+1
      DO 130 I=1,N
      XT=0.3*XC(I) + 0.7*X(I)
  120 OLDX(I)=X(I)
  130 X(I)=XT
```

```
C...  SAVE VALUES OF NORM AND EV
 200  NORML=NORM
      EVL=EV
      RETURN
      END
```

APPENDIX B. TWO-PHASE MODEL COMPUTER PROGRAM

The two-phase bubbling bed model of the NC State gasifier is a Fortran program. The components of the program and a brief description of the function of each are listed below.

BUB - main program. coordinates overall iterative calculational procedures, and handles input/output operations.

BLOCK - block data subprogram. stores gas physical property data, etc.

RXN - coordinates iterative procedure for each step in the fluidized bed

JET - calculates hydrodynamics and mass transfer coefficients for jet region of bed

HYDRO - calculates hydrodynamics for fluidized region of bed

ERATES - calculates reaction rates in emulsion phase

BRATES - calculates reaction rates in bubble phase

WSHIFT - calculates extent of water gas shift reaction necessary to achieve equilibrium

SSHIFT - adjusts gas flow rates to achieve equilibrium of sulfur shift reaction ($H_2S + CO_2 = COS + H_2O$)

COEFF - calculates mass transfer coefficients in fluidized region of the bed

MATBAL - performs species mass balances

FCORR - adjusts bubble and emulsion gas flows when emulsion flow is greater than the minimum fluidization flow

ATTRIT - calculates attrition rate and adjusts size distribution of particles in bed

ELUT - calculates elutriation rate from the bed and size distributions of elutriates and spent char

VTERM - calculates particle terminal velocities

FREE - performs calculations for freeboard region of reactor

GILDEV - determines devolatilization product yields

BLOW - calculates rate and composition of feed coal blown out of reactor

MIX - calculates mixture flow rates and temperature when two gas streams are combined

HTRXN - calculates heat of reaction when given flow rates of reactants and products

EBAL - performs energy balance around reactor

VIS - calculates viscosity of gas mixtures

TCON - calculates thermal conductivity of gas mixtures

GDIFF - calculates binary gas diffusivities

BEDTEM - determines bed temperature at any height for specified bed temperature profile

As discussed previously, several options were built into the model. The options are a part of the required input, and are summarized below.

TOPT - bed temperature option
    0 = specified isothermal temperature
    1 = isothermal bed temperature determined from energy balance calculations
    2 = specified temperature profile

JOPT - jet option
    0 = neglect jet region
    1 = jet region included

DOPT - devolatilization option
    0 = no devolatilization (for char feed)
    1 = include devolatilization

SOPT - sulfur gas production option
    0 = calculate sulfur gas production rate by equating sulfur and carbon conversions
    1 = use Yergey-Vestal kinetics

WOPT - water gas shift reaction option
    0 = assume equilibrium
    1 = use shift kinetics

EOPT - elutriation option
    0 = neglect elutriation
    1 = include elutriation

NP - print option, specifies printing of data every NPth step in the bed

HN - stepsize for bed calculations, ft

DELHF - stepsize for freeboard calculations, ft

Four of the input parameters to the model are dependent on the material being gasified. These inputs are:

FOC - char reactivity factor, defined by equation (36)

FWGC - shift reactivity factor, defined by equation (42)

AC - CO/CO_2 combustion product coefficient, defined by equation (18). for AC=0, equation (19) is used

KAT - char abrasion constant, defined by equation (70)

The remaining required inputs to the model are listed below.

TITLE - comment string. maximum of 40 characters

FCOAL - coal feed rate, lb/hr

FH2O - steam feed rate, lb/hr

FO2 - oxygen feed rate, scfm

FN2 - nitrogen feed rate, scfm

FPN2 - purge nitrogen feed rate, scfm

XCO(i) - ultimate analysis of feed coal, wt fractions 1=C, 2=H, 3=O, 4=N, 5=S, 6=ash

XP(i) - proximate analysis of feed coal, wt fractions 1=fixed C, 2=moisture, 3=vol matter, 4=ash

PSIG - reactor pressure, psig

TOC - coal pretreatment temperature (if any), °F

SDEN - particle density of feed coal, lb/ft^3

TCOAL - temperature of feed coal, °F

TGAS - temperature of feed gas, °F

TPN2 - temperature of purge nitrogen, °F

DIA - diameter of fluidized bed, in

HT - height of fluidized bed, in

HF - height of freeboard region of reactor, ft

DOR - diameter of feed gas nozzle(s), ft

NOR - number of feed gas nozzles

S(i) - feed coal sieve analysis, wt fractions. assumes use of US Standard Sieves 12,20,30,40,60,80,100,200,230, and pan.

FC - initial estimate of fractional carbon conversion

TS - specified bed temperature for TOPT=0, initial estimate of bed temperature for TOPT=1, not used for TOPT=2

TL(i) - thermocouple positions in bed, inches above feed nozzles (used only for TOPT=2)

TEMP(i) - temperatures at locations specified by TL(i), °F (used only for TOPT=2)

Source code listings for the program are given in the following pages.

```
C**********************************************************************
C     MAIN PROGRAM FOR BUBBLING BED MODEL OF THE NCSU
C     FLUIDIZED BED COAL GASIFICATION REACTOR.
C**********************************************************************
      dimension title(10),xc(6),tl(5),temp(5),fe(9),fb(9),xco(6),xd(6),
     *        ye(9),yb(9),yt(9),fin(9),fout(9),xp(4),sd(10),
     *        s(10),sc(10),dp(10),mw(9),gnam(9),yd(9),fex(9),fd(9),
     *        se(10),dc(10),xtar(6),sb(10),xb(6),enam(6)
      integer topt,dopt,sopt,wopt,eopt
      common/blk2/toc,foc,fwgc,ac
      common/blk4/tl,temp
      common/blk6/cvol,cmass
      common/dat1/mw
      common/dat5/dp
      common/dat8/gnam,enam
      common/dat9/xtar
      real nor,mcc,mw,kat
      open(unit=1,name='bub.dat',type='old')
      open(unit=2,name='bub2.out',type='new')
    5 ibigc=0
C-----READ ALL NEEDED INPUT DATA
      read(1,10,end=1000)(title(i),i=1,10)
   10 format(10a4)
      open(unit=4,name='bub4.out',type='new')
      read(1,20)fcoal,fh2o,fo2,fn2,fpn2
   19 format(10f8.0)
   20 format(8f10.0)
   21 format(7i5)
      read(1,20)(xco(i),i=1,6)
      read(1,20)(xp(i),i=1,4)
      read(1,20)(tl(i),i=1,5)
      read(1,20)(temp(i),i=1,5)
      read(1,20)foc,fwgc,ac
      read(1,20)psig,toc,sden,tgas,tcoal,tpn2
      read(1,20)dia,ht,dor,nor
      read(1,19)(s(i),i=1,10)
      read(1,20)hf,delhf,hn,fc,ts
      read(1,21)np,topt,jopt,dopt,sopt,wopt,eopt
      read(1,20)kat
C-----CALCULATE BED CROSS-SECTIONAL AREA
      abed=3.1416*(dia/24.)**2
C-----CALCULATE INLET CARBON FLOW, LB/HR
      qocc=fcoal*xco(1)
C-----CALCULATE AVERAGE FEED PARTICLE DIAMETER, FT
      pdia=0.0
      do 18 i=1,10
   18 pdia=pdia+s(i)*dp(i)
C-----CONVERSION TO PROPER UNITS
      p=psig+14.696
      tcoal=tcoal+459.7
      tgas=tgas+459.7
      tpn2=tpn2+459.7
      ts=ts+459.7
      toc=toc+459.7
      h=ht/12.0
      d=dia/12.0
      fpn2=fpn2/359.0
      do 16 i=1,9
      fin(I)=0.0
   16 continue
      fin(1)=fo2/359.0
      fin(6)=fn2/359.0
      fin(9)=fh2o/(18.02*60.0)
```

```
C-----ESTIMATE COAL SIZE DISTRIBUTION AND COMPOSITION AT BED INLET
      do 17 i=1,10
      dc(i)=0.5*dp(i)
      sd(i)=s(i)
  17  continue
      ad=fcoal*(xp(1)+xp(4))
      xd(1)=fcoal*xp(1)/ad
      xd(2)=0.0
      xd(3)=0.0
      xd(4)=fcoal*xco(4)/ad
      xd(5)=xco(5)
      xd(6)=1.0-xd(1)-xd(2)-xd(3)-xd(4)-xd(5)
      fc=(fc*xco(1)-xco(1)+xp(1))/xp(1)
      fs=fc
      fs2=fs
c-----CALCULATE FEED VOL MATTER CONTENT, DRY WT % (FOR HEAT CAP EQNS)
      vm=xp(3)*100.0/(1-xp(2))
C-----ESTIMATE COAL SIZE DISTRIBUTION AND COMPOSITION IN BED
  22  open(unit=3,name='bub1.out',type='new')
      it=0
      htot=0.0
      dpa=0.0
      do 23 i=1,10
  23  dpa=dpa+sd(i)*dc(i)
      ac=ad*(1.0-xd(1)*fc-xd(5)*fs)
      xc(1)=ad*xd(1)*(1.0-fc)/ac
      xc(2)=ad*xd(2)/ac
      xc(3)=ad*xd(3)/ac
      xc(4)=ad*xd(4)/ac
      xc(5)=ad*xd(5)*(1.0-fs)/ac
      xc(6)=ad*xd(6)/ac
      tb=tgas
      te=tgas
      kkk=1
C-----ASSUME FEED GASES SPLIT EVENLY INTO BUBBLE AND EMULSION PHASES
      do 26 i=1,9
      fe(i)=0.5*fin(i)
      fb(i)=fe(i)
  26  continue
c
      write(3,28)(title(i),i=1,10)
  28  format('1',10x,10a4,///)
      write(3,30)(gnam(i),i=1,9)
  30  format('0',///40X,'GAS FLOW RATES AND COMPOSITION',//1X,'HT(FT)',
     1  1X,'TS,TE,TB(R)',8X,9(a4,6x),'TOT',/)
      write(3,31)htot,tgas,(fin(i),i=1,9)
  31  format(1x,f5.2,f10.1,3x,'F =',9f10.6,/)
C-----BEGIN STEP-BY-STEP CALCULATIONS THRU BED REGION OF REACTOR
      ctot=0.0
      rorg3t=0.0
      rfest=0.0
  35  htot=htot+hn
      call rxn(ts,te,tb,p,fe,fb,ac,xc,fc,fs,fs2,rorg3,rfes,dpa,sden,
     *         topt,jopt,sopt,wopt,dor,nor,d,abed,htot,hn,hjet,it)
      ctot=ctot+cmass
      rorg3t=rorg3t+rorg3
      rfest=rfest+rfes
      if(htot.eq.hn) tbot=ts
      if(kkk.ne.np) go to 47
      fetot=0.0
      fbtot=0.0
      do 38 k=1,9
      fetot=fetot+fe(k)
```

```
 38  fbtot=fbtot+fb(k)
     ftot=fetot+fbtot
     do 40 k=1,9
     ye(k)=fe(k)/fetot
     yb(k)=fb(k)/fbtot
     yt(k)=(fe(k)+fb(k))/ftot
 40  continue
     write(3,42)htot,ts,(fe(j),j=1,9),fetot
 42  format(1x,f5.2,3x,f7.1,3x,'FE=',10F10.6)
     write(3,43)(fb(j),j=1,9),fbtot
 43  format(19x,'FB=',10F10.6)
     write(3,44)te,(ye(k),k=1,9)
 44  format(9x,f7.1,3x,'YE=',9F10.4)
     write(3,45)(yb(k),k=1,9)
 45  format(19x,'YB=',9F10.4)
     write(3,46)tb,(yt(k),k=1,9)
 46  format(9x,f7.1,3x,'YT=',9F10.4,/)
     kkk=0
 47  kkk=kkk+1
     if(htot.lt.h) go to 35
c
     write(3,48)
 48  format(/19x,'YE=EMULSION PHASE MOLE FRACTION',5x,'FE=EMULSION
    * PHASE FLOW RATE, LBMOLE/MIN',/19x,'YB=BUBBLE PHASE MOLE
    * FRACTION',7x,'FB=BUBBLE PHASE FLOW RATE, LBMOLE/MIN',/19x,
    * 'YT=OVERALL MOLE FRACTION')
C-----SUBROUTINE MIX COMBINES THE EMULSION AND BUBBLE PHASES
     call mix(fe,fb,te,tb,0.0,fout,tgout)
C-----SUBROUTINE ATTRIT CALCULATES SIZE REDUCTION OF BED SOLIDS
     time=ctot/qc
     call attrit(qc,qd,sd,time,kat,dc)
C-----SUBROUTINE ELUT CALCULATES ELUTRIATION RATES FROM THE BED
     call elut(fout,tgout,p,qc,sd,dc,sden,dpa,abed,ertot,
    *       se,sc,dca,dea,eopt)
C-----CALL FREE TO CALCULATE TEMP'S IN FREEBOARD REGION
 50  call free(fcoal,tcoal,xp,xco,xd,qd,sden,s,hf,delhf,p,fout,
    *       fex,fd,tar,tgout,top,dopt,eopt,abed,btot,sd,sb,xb)
c
     fines=ertot+btot
     fcc=(fout(2)+fout(4)+fout(5)+fout(8))*60.0*12.01/(qd*xd(1))
     fsc=(fout(7)+fout(8))*60.0*32.06/(qd*xd(5))
     if(sopt.eq.1) go to 36
     fs2c=fsc
     go to 37
 36  fs2c=3.0*fsc*rfest/(rfest+rorg3t)
 37  write(4,49)fc,fcc,fs,fsc,fs2,fs2c
 49  format(/3x,'fc,fcc=',2f9.4,5x,'fs,fsc=',2f9.4,5x,'fs2,fs2c='2f9.4)
c
     if(topt.eq.0.or.topt.eq.2) go to 51
C-----EBAL IS CALLED FOR AN ENERGY BALANCE
     call ebal(fcoal,qc,fines,fin,fpn2,fex,tcoal,tgas,tpn2,ts,top,
    *          top,vm,ediff)
     write(4,56)ts,ediff
 56  format(10x,'ts=',f7.1,5x,'ediff=',e13.4)
c
C-----CHECK ENERGY BALANCE AND CONVERSION ESTIMATE
 51  ibig=ibig+1
     if(ibig.ge.10) stop
     if(abs(ediff).gt.1.0) go to 60
     ibig=0
     ibigc=ibigc+1
     if(ibigc.lt.10) go to 41
     write(2,39)(title(i),i=1,10)
 39  format('1',5x,10a4,/,5x,'iteration on c conv failed.')
     close(unit=3,disp='save')
     close(unit=4,disp='save')
     go to 5
 41  write(3,52)ibigc
 52  format(//5x,i2,' iterations required',/)
     if(abs(fc-fcc).gt.(0.01*fcc)) go to 53
     if(sopt.eq.0) go to 190
     if(abs(fs-fsc).le.(0.01*fsc)) go to 190
     if(ibigc.ge.10) go to 190
C-----USE WEGSTEIN'S METHOD TO GET NEW CONVERSION ESTIMATE
 53  if(ibigc.eq.1) go to 54
     xx=(fcco*(fc-fco)-fco*(fcc-fcco))/(fc-fco-fcc+fcco)
     yy=(fsco*(fs-fso)-fso*(fsc-fsco))/(fs-fso-fsc+fsco)
     zz=(fs2co*(fs2-fs2o)-fs2o*(fs2c-fs2co))/(fs2-fs2o-fs2c+fs2co)
     go to 55
 54  xx=0.5*fc + 0.5*fcc
     yy=0.8*fs + 0.2*fsc
     zz=0.8*fs2+ 0.2*fs2c
C-----SAVE OLD VALUES
 55  if(xx.ge.1.0) xx=0.9999
     if(yy.ge.1.0) yy=0.9999
     if(zz.ge.1.0) zz=0.9999
     if(xx.le.0.0) xx=0.05
     if(yy.le.0.0) yy=0.05
     if(zz.le.0.0) zz=0.05
     fco=fc
     fcco=fcc
     fc=xx
     fso=fs
     fsco=fsc
     fs=yy
     fs2o=fs2
     fs2co=fs2c
     fs2=zz
     if(sopt.eq.0) fs=fc
     go to 85
C-----NEW TEMPERATURE ESTIMATE (WEGSTEIN'S METHOD)
 60  if(ibig.eq.1) go to 70
     xx=ts-ediff*((ts-tso)/(ediff-ediffo))
     go to 75
 70  xx=ts-2.0*ediff
C-----SAVE OLD VALUES
 75  if(xx.gt.2360.) xx=2360.
     if(xx.lt.1860.) xx=1860.
     tso=ts
     ediffo=ediff
     ts=xx
C-----CLOSE AND DELETE OLD OUTPUT FILE
 85  close(unit=3,disp='delete')
     go to 22
C-----COMBINE BED ELUTRIATES AND BLOWNOVER SOLIDS
190  if(fines.le.0.0) go to 191
     do 192 i=1,6
     xb(i)=(ertot*xc(i)+btot*xb(i))/fines
192  continue
     dba=0.0
     do 193 i=1,10
193  dba=dba+sb(i)*dp(i)
     dfa=(btot*dba+ertot*dea)/fines
191  write(3,201)
201  format(////t40,'PARTICLE SIZE DISTRIBUTIONS',//12x,
    *  'Wt Fraction/Size,ft',78x,'Avg(ft)')
```

```
      write(3,202)(s(i),i=1,10),(dp(i),i=1,10),pdia
 202  format(/2x,'Feed',10f10.5,/6x,11f10.5)
      write(3,203)(sc(i),i=1,10),(dc(i),i=1,10),dca
 203  format(/2x,'Char',10f10.5,/6x,11f10.5)
      write(3,204)(se(i),i=1,10),(dc(i),i=1,10),dea
 204  format(/2x,'Elut',10f10.5,/6x,11f10.5)
      write(3,205)(sb(i),i=1,10),(dp(i),i=1,10),dba
 205  format(/2x,'Blow',10f10.5,/6x,11f10.5)
C-----PRINT RESULTS (THIS SECTION WRITES TO BUB2.OUT, AND IS
C-----FORMATTED FOR THE REPORT-QUALITY PRINTER
      write(2,102)(title(i),i=1,10)
 102  format('1',/////,t38,10a4,///t38,'REACTOR SPECIFICATIONS'/)
      xx=p*101.325/14.696
      write(2,104)xx,psig
 104  format(t30,'Pressure',t50,f6.1,' kPa (',f5.1,' psig)')
      xx=dia/39.37
      write(2,108)xx,dia
 108  format(t30,'Bed Diameter',t50,f5.2,' m (',f4.1,' in)')
      xx=ht/39.37
      write(2,110)xx,ht
 110  format(t30,'Bed Height',t50,f5.2,' m (',f4.1,' in)')
      xx=hf/3.28
      write(2,111)xx,hf
 111  format(t30,'Freeboard Height',t50,f5.2,' m (',f4.1,' ft)')
      xx=fcoal*0.4536
      write(2,134)xx,fcoal
 134  format(/t30,'Coal',t40,f6.2,' kg/hr (',f5.2,' lb/hr)')
      xx=fh2o*0.4536
      write(2,136)xx,fh2o
 136  format(t30,'Steam',t40,f6.2,' kg/hr (',f5.2,' lb/hr)')
      yy=fo2*32.*60.0/359.0
      write(2,138)fo2,yy
 138  format(t30,'Oxygen',t40,f6.2,' SCFM (',f5.2,' lb/hr)')
      yy=fn2*28.01*60.0/359.0
      write(2,140)fn2,yy
 140  format(t30,'Nitrogen',t40,f6.2,' SCFM (',f5.2,' lb/hr)')
      fpn2=fpn2*359.0
      yy=yy*fpn2/fn2
      write(2,142)fpn2,yy
 142  format(t30,'Purge N2',t40,f6.2,' SCFM (',f5.2,' lb/hr)')
      tcoal=tcoal-459.7
      xx=(tcoal-32.0)/1.8
      write(2,146)xx,tcoal
 146  format(/t30,'Coal Feed Temp',t47,f6.1,' C (',f6.1,' F)')
      tgas=tgas-459.7
      xx=(tgas-32.)/1.8
      write(2,148)xx,tgas
 148  format(t30,'Gas Feed Temp',t47,f6.1,' C (',f6.1,' F)')
      tpn2=tpn2-459.7
      xx=(tpn2-32.)/1.8
      write(2,149)xx,tpn2
 149  format(t30,'Purge N2 Temp',t47,f6.1,' C (',f6.1,' F)')
      write(2,116)
 116  format(//t38,'SOLID FEED PROPERTIES'/)
      xx=sden/62.43
      write(2,118)xx,sden
 118  format(t30,'Particle Density',t51,f5.3,' g/cc (',f5.1,' lb/cf)')
      pdia=pdia*12.0
      yy=pdia*25.4
      write(2,122)yy,pdia
 122  format(t30,'Avg Particle Diameter',f7.3,' mm (',f6.4,' in)')
      write(2,126)
 126  format(/t31,'Proximate Analysis',t57,'Ultimate Analysis')
```

```
      write(2,127)xp(1),xco(1)
 127  format(t30,'Fixed Carbon',f8.4,t60,'C',f10.4)
      write(2,128)xp(3),xco(2)
 128  format(t30,'Vol. Matter',f9.4,t60,'H',f10.4)
      write(2,129)xp(2),xco(3)
 129  format(t30,'Moisture',f12.4,t60,'O',f10.4)
      write(2,130)xp(4),xco(4)
 130  format(t30,'Ash',f17.4,t60,'N',f10.4)
      write(2,131)xco(5),xco(6)
 131  format(t60,'S',f10.4/t60,'Ash',f8.4)
      write(2,133)foc
 133  format(//t34,'MODEL PARAMETERS & OPTIONS',//t30,'Coal
     * Reactivity',t55,f6.3)
      if(wopt.eq.1) write(2,150)fwgc
 150  format(t30,'Shift Reactivity',t56,e10.4)
      if(ac.eq.0.0) write(2,151)
 151  format(t30,'CO/CO2 Coefficient',t56,'Arthur Eqn.')
      if(ac.ne.0.0) write(2,157)ac
 157  format(t30,'CO/CO2 Coefficient',t56,f5.3)
      write(2,147)kat
 147  format(t30,'Abrasion Constant',t56,e10.4)
      write(2,152)topt,jopt
 152  format(/t30,'Topt = ',i1,t60,'Jopt = ',
     *   i1,/t32,'0: isothermal, no e-bal',t62,'0: no jets',/t32,
     *   '1: isothermal, with e-bal',t62,'1: jets',/t32,
     *   '2: imposed temp profile',/t32,'3: adiabatic')
      write(2,153)dopt,sopt
 153  format(t30,'Dopt = ',i1,7x,'0: no devol;  1: devol',/t30,
     *   'Sopt = ',i1,7x,'0: S Conv = C Conv;  1: Y-V Kinetics')
      write(2,154)wopt,eopt
 154  format(t30,'Wopt = ',i1,7x,'0: shift equil;  1: shift kinetics',
     *   /t30,'Eopt = ',i1,7x,'0: no elut;  1: elut')
      write(2,155)hn,delhf
 155  format(/t30,'Bed Increment',t55,f5.3,' ft',/t30,
     *     'Freeboard Increment',t55,f5.3,' ft')
      write(2,159)(title(i),i=1,10)
      fotot=0.0
      fdtot=0.0
      fextot=0.0
      fex(6)=fex(6)+fpn2/359.0
      do 172 i=1,9
      fotot=fotot+fout(i)
      fdtot=fd(i)+fdtot
 172  fextot=fex(i)+fextot
      fexdry=fextot-fex(9)
      do 174 i=1,9
      ye(i)=fout(i)/fotot*100.
      yb(i)=fd(i)/fdtot*100.
      yt(i)=fex(i)/fextot*100.
      yd(i)=fex(i)/fexdry*100.
 174  continue
      yd(9)=0.0
      scfm=359.0*fextot
      scfmd=359.0*fexdry
 159  format('1',//////t38,10a4)
      write(2,156)
 156  format(/t45,'MODEL OUTPUT',//)
      yy=scfm*60.0/359.0
      write(2,158)yy,scfm
 158  format(t30,'Gas Flow Rate (wet)',t52,f5.3,' lbmol/hr (',
     *     f5.2,' SCFM)')
      yy=scfmd*60.0/359.0
      write(2,160)yy,scfmd
 160  format(/t30,'Gas Flow Rate (dry)',t52,f5.3,' lbmol/hr (',
     *     f5.2,' SCFM)')
      if(jopt.eq.1) write(2,161)hjet
 161  format(/t30,'Jet Height',t52,f4.2,' ft')
      write(2,162)ctot
 162  format(/t30,'Solids Holdup',t52,f5.2,' lbs')
      xx=(fout(2)+fout(4)+fout(5)+fout(8))*60.0*12.01/qocc
      yy=(fex(2)+fex(4)+fex(5)+fex(8))*60.0*12.01/qocc
      zz=yy-xx
      write(2,163)zz,xx,yy
 163  format(/t30,'Carbon Conversion',t52,'Devolatilization',t72,f5.3,
     *    /t52,'Comb./Gas.',t72,f5.3,/t52,'Total',t72,f5.3)
      write(2,176)
 176  format(//t39,'BED EXIT GAS',t69,'DEVOL. GAS',//t33,
     *    'lbmoles/min',4x,'mole %',t63,'lbmoles/min',4x,'mole %',/)
      do 180 i=1,9
      write(2,178)gnam(i),fout(i),ye(i),fd(i),yb(i)
 178  format(t24,a4,f14.5,f12.4,8x,f10.5,f12.4)
 180  continue
      write(2,182)fotot,fdtot
 182  format(t24,'Total',f13.5,20x,f10.5)
C-----PRINT PREDICTED GAS COMPOSITION AND PRODUCTION RATES
      write(2,164)
 164  format(//t45,'REACTOR EXIT GAS'//t34,'% Wet',5x,'% Dry',6x,
     1    'kg/hr',7x,'lb/hr',6x,'g/kg Feed'/)
      term=scfm*60.0/359.
      do 168 i=1,9
      xx=term*yt(i)/100.0*mw(i)
      yy=xx*0.4536
      zz=xx/fcoal*1000.0
      write(2,166)gnam(i),yt(i),yd(i),yy,xx,zz
 166  format(t24,a4,2x,2f10.4,1pe12.2,2e12.2)
 168  continue
      write(2,159)(title(i),i=1,10)
      write(2,400)qd,qc,fines,tar
 400  format(//t45,'SOLIDS',//t30,'Bed Inlet',4x,'Reactor Exit',
     *    4x,'Cyclone Dust',7x,'Tar',/t29,4(f5.2,' lb/hr',4x))
      top=top-459.7
      ts=ts-459.7
      tbot=tbot-459.7
      write(2,407)ts,tbot,top,top
 407  format(t30,4(f6.1,' F',7x))
      pdia=pdia/12.0
      write(2,408)pdia,dca,dfa
 408  format(t29,3(f7.5,' ft',5x),/)
      do 402 i=1,6
      write(2,401)enam(i),xd(i),xc(i),xb(i),xtar(i)
 401  format(t25,a4,2x,4(f6.4,9x))
 402  continue
c
      close(unit=3,disp='save')
      close(unit=4,disp='save')
      go to 5
 1000 stop
      end
      block data
c***********************************************************************
c     a,b,c,d: constants in gas heat capacity eqn
c     dh: heats of reaction, btu/lbmole
c     mw: molecular weights
c     g:  gravitational constant, ft/s**2
c     dp: particle diameters, ft
c     hf: heats of formation, btu/lbmole
c     vc,tc,zc: critical volume (cc/gmol), temperature (K), and
c              compressibility
c     xtar: ultimate analysis of NM coal tar, wt fractions
c***********************************************************************
      real mw
      dimension a(9),b(9),c(9),d(9),dh(20),mw(9),dp(10),
     *          tc(9),vc(9),zc(9),hf(9),gnam(9),enam(6),xtar(6)
      common/dat1/mw
      common/dat2/a,b,c,d
      common/dat3/dh
      common/dat4/g
      common/dat5/dp
      common/dat6/tc,vc,zc
      common/dat7/hf
      common/dat8/gnam,enam
      common/dat9/xtar
      data a/6.713,7.373,6.483,4.598,4.728,7.440,7.629,5.629,7.701/
      data b/-4.88E-7,-1.706E-3,1.231E-3,6.917E-3,9.744E-3,-1.8E-3,
     *   1.906E-4,1.059E-2,2.553E-4/
      data c/1.287E-6,2.056E-6,-1.018E-6,8.82E-7,-4.129E-6,1.975E-6,
     *   1.793E-6,-5.172E-6,7.78E-7/
      data d/-4.362E-10,-5.207E-10,3.131E-10,-4.635E-10,7.025E-10,
     *      -4.784E-10,-4.818E-10,1.005E-9,-1.473E-10/
      data dh/5.65E4,-3.22E4,1.22E4,-1.77E4,-4.76E4,-1.69E5,-2.43E5,
     *       -2.08E5,-1.73E5,7.43E4,0,-2.88E3,0,0,0,0,-2.88E3,
     *       -2.43E5,-2.08E5,-1.73E5/
      data mw/32.00,28.01,2.02,16.04,44.01,28.01,34.08,60.07,18.02/
      data g/32.174/
      data dp/6.07e-3,4.18e-3,2.38e-3,1.68e-3,1.11e-3,7.05e-4,5.41e-4,
     *       3.69e-4,1.97e-4,7.38e-5/
      data vc/73.4,93.1,65.0,99.0,94.0,89.5,98.5,140.0,56.0/
      data tc/154.6,132.9,33.2,190.6,304.2,126.2,373.2,375.0,647.3/
      data zc/0.288,0.295,0.305,0.288,0.274,0.290,0.284,0.260,0.229/
      data hf/0.0,-4.760e4,0.0,-3.223e4,-1.695e5,0.0,8.676e3,
     *       -5.960e4,-1.041e5/
      data gnam/'O2  ','CO  ','H2  ','CH4 ','CO2 ','N2  ','H2S ',
     *        'COS ','H2O '/
      data enam/'C   ','H   ','O   ','N   ','S   ','Ash '/
      data xtar/0.85,0.05,0.08,0.01,0.01,0.00/
c
      end
      subroutine rxn(t,te,tb,p,fe,fb,qc,xc,fc,fs,fs2,rorg3,rfes,dpa,
     *   sden,topt,jopt,sopt,wopt,dor,nor,dia,abed,htot,hn,hjet,itb)
c*********************************************************************
c     SUBROUTINE RXN COORDINATES THE CALCULATIONS WITHIN
c     EACH STEP TAKEN IN THE FLUIDIZED BED
c*********************************************************************
      dimension fe(9),fb(9),xc(6),ye(9),yb(9),rate(20),fec(9),fbc(9),
     *  feo(9),fbo(9),diff(9),dere(2,9),derb(2,9),k(9),fel(9),fbl(9)
      integer topt,sopt,wopt
      real nor,k
      call bedtem(htot,t,te,tb,topt)
      it=0
      itb=itb+1
C-----STORE INLET FLOW RATES AND TEMPS TO COMPARTMENT
      do 2 i=1,9
      feo(i)=fe(i)
      fbo(i)=fb(i)
    2 continue
      teo=te
      tbo=tb
      te=t
    5 it=it+1
C-----CALCULATE BUBBLE AND EMULSION PHASE MOLE FRACTIONS
      fbtot=0.0
      fetot=0.0
      do 10 i=1,9
      if(fe(i).le.0.0) fe(i)=0.0
      if(fb(i).le.0.0) fb(i)=0.0
      fetot=fetot+fe(i)
   10 fbtot=fbtot+fb(i)
      do 20 i=1,9
      ye(i)=fe(i)/fetot
      yb(i)=fb(i)/fbtot
   20 continue
c
      if(jopt.eq.0) go to 24
      if(htot.gt.hjet.and.itb.gt.1) go to 24
      call jet(t,te,tb,p,fe,fb,ye,yb,qc,dor,nor,dpa,sden,
     *      gden,s,abed,hn,htot,hjet,k)
      go to 26
c
   24 call hydro(t,te,tb,p,fe,fb,ye,yb,qc,diff,dia,abed,hn,
     *      dpa,sden,gden,s,k)
c
   26 call erates(t,te,p,ye,fe,fc,fs,fs2,rorg3,rfes,s,dpa,
     *      gden,xc,sopt,wopt,rate)
c
      call brates(te,tb,p,ye,yb,fb,wopt,rate,diff,k)
c
      call matbal(te,tb,feo,fbo,rate,diff,fec,fbc)
c
      call fcorr(te,tb,p,fec,fbc,diff)
c
C-----DETERMINE DERIVATIVES
      if(it.ne.2) go to 37
      do 30 i=1,9
      dere(1,i)=dere(2,i)
      derb(1,i)=derb(2,i)
   30 continue
   37 do 40 i=1,9
      dere(2,i)=(fec(i)-feo(i))/hn
      derb(2,i)=(fbc(i)-fbo(i))/hn
   40 continue
```

```
C-----DETERMINE FLOWS AND TEMPS AT NEXT POSITION
      do 43 i=1,9
      fel(i)=fe(i)
      fbl(i)=fb(i)
   43 continue
      if(it.gt.1) go to 50
      do 45 i=1,9
      fe(i)=fec(i)
      fb(i)=fbc(i)
   45 continue
      go to 70
   50 do 60 i=1,9
      fe(i)=feo(i)+(dere(1,i)+dere(2,i))*hn/2.0
      fb(i)=fbo(i)+(derb(1,i)+derb(2,i))*hn/2.0
   60 continue
      if(it.ge.10) go to 305
   70 do 75 i=1,9
      if(abs(fe(i)-fel(i)).gt.(0.01*fel(i))) go to 5
   75 if(abs(fb(i)-fbl(i)).gt.(0.01*fbl(i))) go to 5
C-----CHECK FOR NEGATIVES, CORRECT IF FOUND
  305 do 310 i=1,9
      if(fe(i).le.0.0) fe(i)=0.0
  310 if(fb(i).le.0.0) fb(i)=0.0
c
      return
      end
      subroutine bedtem(ht,t,te,tb,i)
c*********************************************************************
c     SUBROUTINE BEDTEM DETERMINES THE TEMPERATURE AT ANY
c     HEIGHT IN THE BED FOR A SPECIFIED TEMPERATURE PROFILE
c
c     i is a parameter which specifies the mode of temperature
c     determination:  i=0 for isothermal bed, no energy balance
c                     i=1 isothermal, use energy balance to iterate
c                         for proper temperature
c                     i=2 imposed temp profile, no energy balance
c*********************************************************************
      dimension tl(5),temp(5)
      common/blk4/tl,temp
      if(i.le.1) go to 30
      if(i.eq.2) go to 5
      if(i.eq.3) return
C-----FOR I=2 LINEAR INTERPOLATION AND EXTRAPOLATION ARE USED TO
C-----DETERMINE THE TEMPERATURE AT HEIGHT H.
    5 h=ht*12.0
      if(h.gt.tl(2)) go to 10
      t=temp(1)+((temp(2)-temp(1))/(tl(2)-tl(1)))*(h-tl(1))+459.7
      go to 30
   10 if(h.gt.tl(3)) go to 20
      t=temp(2)+((temp(3)-temp(2))/(tl(3)-tl(2)))*(h-tl(2))+459.7
      go to 30
   20 t=temp(3)+((temp(4)-temp(3))/(tl(4)-tl(3)))*(h-tl(3))+459.7
   30 te=t
      tb=t
c
      return
      end
      subroutine jet(t,te,tj,p,fe,fj,ye,yj,qc,dor,nor,
     *     dpa,sden,dene,s,abed,hn,htot,hjet,k)
c**********************************************************************
c     SUBROUTINE JET CALCULATES THE HYDRODYNAMICS OF THE
c     JET REGION OF THE FLUIDIZED BED AND THE JET-EMULSION
c     MASS TRANSFER COEFFICIENTS
c**********************************************************************
      dimension fe(9),fj(9),ft(9),ye(9),yj(9),mw(9),k(9)
      common/blk5/qe,qb
      common/blk6/cvol,cmass
      common/blk7/uo,umf,emf,ub,dbub,bvol
      common/dat1/mw
      common/dat4/g
      real mw,mwe,mwj,nor,k
c
C-----CALCULATE VOIDAGE IN EMULSION PHASE
      emf=0.449+145.0*dpa
C-----CALC AVG MOL WT'S, DENSITIES, AND TOTAL FLOWS
      mwe=0.0
      mwj=0.0
      fetot=0.0
      fjtot=0.0
      do 5 i=1,9
      mwe=mwe+ye(i)*mw(i)
      mwj=mwj+yj(i)*mw(i)
      ft(i)=fe(i)+fj(i)
      fetot=fetot+fe(i)
    5 fjtot=fjtot+fj(i)
      ftot=fetot+fjtot
      qtot=(fetot*te+fjtot*tj)*(14.7/p)*359.0/(492.*60.0)
      uo=qtot/abed
      dene=mwe*p/(10.73*te)
      denj=mwj*p/(10.73*tj)
C-----CALC MIN FLUID VELOCITY
      call vis(te,p,ye,gvis)
      ar=(dene*(sden-dene)*g*dpa**3)/(gvis*gvis)
      umf=gvis/(dene*dpa)*0.0135*ar**0.73
C-----CALC GAS ORIFICE VELOCITY (ONLY AT GAS INLET)
      if(htot.gt.hn) go to 10
      area=nor*3.1416*(dor/2.0)**2
      uo=qtot/area
C-----CALC JET PENETRATION HEIGHT AND JET HALF-ANGLE
      hjet=dor*5.2*(denj*dor/(sden*dpa))**0.3
     1     *(1.3*(uo*uo/(g*dor))**0.2-1)
      tan=0.096*(sden*dpa/(denj*dor))**0.3
C-----CHECK JET ANGLE TANGENT (TAN). MAX TANGENT IS SET
c     by cone configuration: max angle = 19 degrees, max tan = 0.344
      if(tan.gt.0.344) tan=0.344
      yo=0.5*dor/tan
C-----CALC JET AND EMULSION FRACTIONS
   10 diaj=2.0*(htot+yo)*tan
      areaj=nor*3.1416*(diaj/2.0)**2
      areae=emf*(abed-areaj)
      areas=abed-areaj-areae
      cmass=areas*hn*sden
      bvol=areaj*hn
      cvol=areas*hn
      s=6.0*cmass/(sden*dpa)
C-----CALC EMULSION AND SOLIDS VELOCITIES
      us=qc/(3600.*sden*areas)
      ue=umf/emf-us
C-----CALC EMULSION/JET GAS FLOW SPLIT (ONLY AT GAS INLET)
      if(htot.gt.hn) go to 30
      fetot=ue*areae*(492./te)*(p/14.7)*60./359.0
      term=fetot/ftot
      do 20 i=1,9
      fe(i)=term*ft(i)
      fj(i)=ft(i)-fe(i)
  20  continue
c
  30  qe=ue*areae
      fetot=qe*(492./te)*(p/14.7)*60.0/359.0
      fjtot=ftot-fetot
      qb=fjtot*(tj/492.)*(14.7/p)*359.0/60.0
      ub=qb/areaj
      dbub=diaj
C-----CALCULATE COEFFICIENTS FOR JET-EMULSION MASS TRANSFER
      sjet=3.1416*dor*hn
      x=0.48*ub*(g*htot/(ub*ub))**0.504*(dor*ub*denj/gvis)**0.068
     *     *(dor/htot)**0.095
      do 40 i=1,9
      k(i)=x*sjet
  40  continue
c
      return
      end
      subroutine hydro(t,te,tb,p,fe,fb,ye,yb,qc,
     *                  diff,dia,abed,hn,dpa,sden,gden,s,k)
c***********************************************************************
c     SUBROUTINE HYDRO PERFORMS THE CALCULATIONS TO DETERMINE
c     THE HYDRODYNAMIC OF THE FLUIDIZED BED
c***********************************************************************
      dimension fe(9),fb(9),ye(9),yb(9),mw(9),k(9),diff(9)
      common/blk5/qe,qb
      common/blk6/cvol,cmass
      common/blk7/uo,umf,emf,ub,dbub,bvol
      common/dat1/mw
      common/dat4/g
      real mw,mwavg,k
C-----CALCULATE VOIDAGE IN EMULSION PHASE
      emf=0.449+145.0*dpa
C-----DETERMINE DENSITY AND VISCOSITY OF THE EMULSION PHASE GAS
      mwavg=0.0
      do 5 i=1,9
      mwavg=mwavg+ye(i)*mw(i)
    5 continue
      gden=mwavg*p/(10.73*te)
      call vis(te,p,ye,gvis)
C-----CALCULATE MINIMUN FLUIDIZATION VELOCITY, UMF.
      ar=(gden*(sden-gden)*g*dpa**3)/(gvis*gvis)
      umf=gvis/(gden*dpa)*0.0135*ar**0.73
C-----CALCULATE H/HMF RATIO
      fetot=0.0
      fbtot=0.0
      do 10 i=1,9
      fetot=fetot+fe(i)
   10 fbtot=fbtot+fb(i)
      qt=((fetot/60.)*(te/492.)+(fbtot/60.)*(tb/492.))*359.*(14.7/p)
      uo=qt/abed
      if(uo.gt.umf) go to 15
      bef=1.0
      go to 20
   15 bef=1.0+10.978*(uo-umf)**0.738*sden**0.376*dpa**1.006
     1/(umf**0.937*gden**0.126)
   20 gamma=(bef-1.0)/bef
C-----CALCULATE SOLIDS VELOCITY, US
      us=qc/(3600.*sden*abed)
C-----CALCULATE BUBBLE VELOCITY, UB
      ue=umf/emf-us
      ub=(uo-(1.-gamma)*emf*ue)/gamma
C-----CALCULATE COMBINED GAS FLOWS THRU EMULSION AND BUBBLE PHASES
      qb=gamma*ub*abed
      qe=qt-qb
C-----CALCULATE BUBBLE DIAMETER
      dbub=(1.-gamma)*(1.-gamma)*ub*ub/(0.506*g)
      if(dbub.gt.dia) dbub=dia
C-----CALCULATE COAL AND BUBBLE VOLUMES IN COMPARTMENT
      cvol=(1.-emf)*abed*hn/bef
      bvol=gamma*abed*hn
C-----COAL HOLDUP AND EXTERIOR SURFACE AREA ARE CALCULATED
      cmass=sden*cvol
      s=6.0*cmass/(sden*dpa)
C-----DETERMINE MASS TRANSFER COEFFICIENTS (BUBBLE-EMULSION)
      call coeff(te,tb,p,ye,yb,diff,k)
      do 30 i=1,9
      k(i)=k(i)*bvol
   30 continue
      return
      end
      subroutine coeff(te,tb,p,ye,yb,n,kbe)
c**********************************************************************
c     SUBROUTINE COEFF CALCULATES THE BUBBLE-EMULSION
c     MASS TRANSFER COEFFICIENTS
c**********************************************************************
      dimension de(9,9),db(9,9),n(9),ye(9),yb(9),dme(9),dmb(9),kbe(9)
      real n,ntot,kbc,kce,kbe
      common/blk7/uo,umf,emf,ub,dbub,bvol
      common/dat4/g
c
C-----FIND THE BINARY GAS DIFFUSIVITIES
      call gdiff(te,p,de)
      call gdiff(tb,p,db)
C-----CALCULATE MIXTURE DIFFUSIVITIES
      ntot=0.0
      do 10 i=1,9
   10 ntot=ntot+n(i)
      do 40 i=1,9
      denome=0.0
      denomb=0.0
      do 30 j=1,9
      denome=denome+(ye(j)*n(i)-ye(i)*n(j))/de(i,j)
   30 denomb=denomb+(yb(j)*n(i)-yb(i)*n(j))/db(i,j)
      if(denome.eq.0.0) go to 35
      dme(i)=(n(i)-ye(i)*ntot)/denome
   35 if(denomb.eq.0.0) go to 40
      dmb(i)=(n(i)-yb(i)*ntot)/denomb
   40 continue
C-----CHECK FOR NON-POSITIVE DIFFUSIVITIES
      do 45 i=1,9
      if(dme(i).lt.1.0e-5) dme(i)=1.0e-5
      if(dmb(i).lt.1.0e-5) dmb(i)=1.0e-5
   45 continue
C-----CALCULATE MASS-TRANSFER COEFFICIENT FOR EACH GAS
      term1=4.5*umf/dbub
      do 50 i=1,9
C  ---CALCULATE BUBBLE-CLOUD COEFFICIENTS
      kbc=term1+5.85*sqrt(dmb(i))*g**0.25/dbub**1.25
C  ---CALCULATE CLOUD-EMULSION COEFFICIENTS
      kce=6.78*sqrt(emf*dme(i)*ub/dbub**3)
C  ---CALCULATE OVERALL COEFFICIENTS (BUBBLE-EMULSION)
      kbe(i)=1.0/(1.0/kbc+1.0/kce)
   50 continue
c
      return
      end
      subroutine erates(t,te,p,y,fe,fc,fs,fs2,rorg3,rfes,s,dpa,
     *     gden,x,sopt,wopt,rate)
c*****************************************************************
c     SUBROUTINE ERATES CALCULATES THE EMULSION PHASE REACTION RATES
c*****************************************************************
      dimension fe(9),rate(20),y(9),pp(9),x(6)
      common/blk2/toc,foc,fwgc,ac
      common/blk6/cvol,cmass
      integer sopt,wopt
      real ke1,ke2,ke3,ke4
      a=ac
C-----CALCULATE EQUILIBRIUM CONSTANTS
      ke1=exp(-29010.6/t+17.09)
      ke2=exp(17744.4/t-12.23)
      ke3=ke1*ke2
      ke4=exp(8395.2/t-4.29)
C-----DETERMINE TOC, THE MAX TEMP TO WHICH THE COAL
C-----HAS BEEN EXPOSED
      if(t.gt.toc)toc=t
C-----CALCULATE GAS PARTIAL PRESSURES, ATM
      patm=p/14.696
      do 30 i=1,9
      pp(i)=y(i)*patm
   30 continue
C-----CALCULATE JOHNSON RATE CONSTANTS
      rk1=(pp(9)*(exp(9.0201-31705.0/t))*(pp(9)-((pp(2)*
     1    pp(3))/ke1)))/((pp(9)+((exp(-22.216+44787.0/t))
     2    *(1.0+16.35*pp(3)+43.5*pp(2))))**2)
      rk2=((exp(2.6741-33076.0/t))*(pp(3)**2-pp(4)/ke2))/
     1    (1.0+pp(3)*(exp(-10.452+19976.0/t)))
      if((pp(3)+pp(4)).le.0.0.or.pp(9).le.0.0) go to 40
      rk3=((pp(3)**1.5)*(pp(9))*(exp(12.4463-44544.0/t))*
     1    (pp(3)*pp(9)-((pp(4)*pp(2))/ke3)))/
     2    (((pp(3)*(sqrt(pp(9))))+(exp(-6.6696+15198.0/t))
     3    *((sqrt(pp(9))*(pp(3)**1.5))+(0.85*pp(2)*pp(3)*
     4    (sqrt(pp(9))))+(18.62*pp(4)*(sqrt(pp(9))))))**2)
      go to 50
   40 rk3=0.0
   50 continue
C-----CALCULATE JOHNSON KINETIC PARAMETERS ALPHA AND FLC
      if(pp(3).le.0.0) go to 51
      alpha=52.7*pp(3)/(1+54.3*pp(3))+0.521*sqrt(pp(3))*pp(9)/
     1     (1+0.707*pp(9)+0.5*sqrt(pp(3))*pp(9))
      go to 52
   51 alpha=0.0
   52 flc=foc*exp(8467/toc)
C-----CALCULATE JOHNSON REACTION RATES
      term=cmass*x(1)/(12.01*(1.0-fc))
      term=term*flc*(1-fc)**0.667*exp(-alpha*fc*fc)
      rate(1)=term*rk1
      rate(2)=term*rk2
      rate(3)=term*rk3
C-----CALCULATE RATE OF C-CO2 REACTION
      rate(10)=0.0
C-----CALCULATE WATER-GAS SHIFT REACTION RATE
C-----(WOPT=0: EQUILIBRIUM,   WOPT=1: SHIFT KINETICS)
      call wshift(te,fe,shift)
      rate(4)=shift
      if(wopt.eq.0) go to 60
   55 if(y(9).le.0.0) rate(4)=0.0
      if(y(9).le.0.0) go to 60
      term=4.715e8*patm*exp(-25147.4/t)*(y(2)-y(3)*y(5)/(y(9)*ke4))
      shift=cvol*fwgc*term
      if(abs(shift).lt.abs(rate(4))) rate(4)=shift
C-----CALCULATE THE OXYGEN CONSUMPTION RATE
 60   tk=t/1.8
      z=0.0247/(0.178*patm-0.039*(patm-pp(1)))
      term=0.032*z*patm*sqrt(tk)*(3.84/(dpa*tk**0.185)
     1      *(dpa*ue*gden*14.883)**0.37+0.0656/dpa)
      ro2=3.837e-3*pp(1)/(1/term+1.05e-10*sqrt(tk)*exp(22143.9/tk))
C-----CALCULATE THE OXIDATION REACTION RATES
      if(ac.gt.0.0) go to 65
      a=0.5*((2.0+2512.*exp(-11234./t))/(1.0+2512.*exp(-11234./t)))
 65   rate(5)=(2-2*a)/a*ro2*s
      rate(6)=(2*a-1)/a*ro2*s
      rate(7)=0.5*fe(2)
      rate(8)=0.5*fe(3)
      rate(9)=2.0*fe(4)
C-----CHECK FOR SUFFICIENT OXYGEN (IF NOT, ADJUST OX RATES)
      o2req=0.5*rate(5)+rate(6)+rate(7)+rate(8)+rate(9)
      if(fe(1).ge.o2req) go to 90
      adjust=fe(1)/o2req
      do 70 i=5,9
      rate(i)=rate(i)*adjust
   70 continue
c-----CALCULATE RATE OF H2S FORMATION
C-----(SOPT=0: ASSUME S CONV = C CONV; SOPT=1: VESTAL/YERGEY KINETICS)
   90 if(sopt.eq.1) go to 100
      rate(11)=(rate(1)+rate(2)+rate(3)+rate(5)+rate(6)+rate(10))*
     *          (x(5)/32.06)/(x(1)/12.01)
      go to 150
  100 rt=1.987*tk
      smass=cmass*x(5)/32.06
      fes=0.333*smass/(1.0-fs)*(1.0-fs2)
      org3=smass-fes
      rorg3=2.5e7*exp(-38100.0/rt)*pp(3)*org3*org3
      rfes=1.8e5*exp(-25100.0/rt)*pp(3)*fes
      rate(11)=rorg3 + rfes
c
  150 return
      end
      subroutine wshift(t,f,sh2)
c*********************************************************************
c     WSHIFT ADJUSTS THE GAS FLOWS, F(I), SO THAT THE WATER-GAS SHIFT
c     RXN IS AT EQUILIBRIUM AT TEMPERATURE T
c
c     t         temperature, rankine
c     kw        the equilibrium constant for the shift reaction
c     root1     one of the two roots for sh2
c     root2     one of the two roots for sh2
c     sh2       degree of the shift reaction toward h2, lbmoles/min
c     term1     used to solve the quadratic equation for sh2
c     term2     used to solve the quadratic equation for sh2
c     f(i)      gas flow rates, lbmoles/min
c**********************************************************************
      dimension f(9)
      real kw
      kw=EXP(8395.2/T-4.29)
      term1=(f(5)+f(3)+(f(2)+f(9))*kw)/(2.*(1.-kw))
      term2=(f(5)*f(3)-kw*f(2)*f(9))/(1.-kw)
      root1=-term1+sqrt(term1**2-term2)
      root2=-term1-sqrt(term1**2-term2)
C-----SELECT THE ROOT OF SMALLER ABSOLUTE MAGNITUDE AS THE MEANINGFUL ROOT
      if(abs(root1)-abs(root2))3,5,5
    3 sh2=root1
      go to 6
    5 sh2=root2
    6 continue
      return
      end
      subroutine brates(te,tb,p,ye,yb,fb,wopt,rate,diff,k)
c***********************************************************************
c     SUBROUTINE CALCULATES THE RATES OF INTERPHASE TRANSPORT FOR EACH
c     GAS COMPONENT AND THE RATES OF THE BUBBLE PHASE REACTIONS.
c***********************************************************************
      dimension rate(20),diff(9),yb(9),ye(9),fb(9),k(9)
      common/blk7/uo,umf,emf,ub,dbub,bvol
      real k,ke
      integer wopt
C-----CALCULATE BUBBLE AND EMULSION MOLAR GAS CONCENTRATIONS
      cetot=p/(10.73*te)
      cbtot=p/(10.73*tb)
C-----CALCULATE RATES OF DIFFUSION INTO BUBBLE PHASE
      do 50 i=1,9
      diff(i)=60.0*(ye(i)*cetot-yb(i)*cbtot)*k(i)
   50 continue
C-----DETERMINE BUBBLE PHASE OXIDATION REACTION RATES
      rate(18)=0.5*fb(2)
      rate(19)=0.5*fb(3)
      rate(20)=2.0*fb(4)
      if((rate(18)+rate(19)+rate(20)).le.fb(1)) go to 60
      rate(18)=fb(1)/3.0
      rate(19)=fb(1)/3.0
      rate(20)=fb(1)/3.0
C-----CALCULATE BUBBLE PHASE SHIFT REACTION RATE
C-----(WOPT=0 FOR EQUIL., WOPT=1 FOR KINETICS)
   60 call wshift(tb,fb,shift)
      rate(16)=shift
      if(wopt.eq.0) return
      ke=exp(8395.2/tb-4.29)
      shift=2.864e15*exp(-79899.0/tb)*cbtot*cbtot*
     *          (yb(2)*yb(9)-yb(5)*yb(3)/ke)*bvol
      if(abs(shift).lt.abs(rate(16))) rate(16)=shift
c
      return
      end
      subroutine matbal(te,tb,fe,fb,rate,diff,fec,fbc)
c*******************************************************************
c     SUBROUTINE MATBAL PERFORMS SPECIES MATERIAL BALANCES
c         te,tb - temperatures, rankine
c         fe,fb - input flows, lbmol/min
c          rate - reaction rates, lbmol/min
c          diff - diffusion rate between e and b phases, lbmol/min
c       fec,fbc - calculated output flow rates, lbmol/min
c******************************************************************
      dimension fe(9),fb(9),rate(20),diff(9),fec(9),fbc(9)
C-----CALCULATE BUBBLE PHASE GAS FLOW RATES (UNCORRECTED)
      fbc(1)=fb(1)-rate(18)-rate(19)-rate(20)+diff(1)
      fbc(2)=fb(2)-2*rate(18)-rate(16)+diff(2)
      fbc(3)=fb(3)-2*rate(19)+rate(16)+diff(3)
      fbc(4)=fb(4)-0.5*rate(20)+diff(4)
      fbc(5)=fb(5)+2*rate(18)+0.5*rate(20)+rate(16)+diff(5)
      fbc(6)=fb(6)+diff(6)
      fbc(7)=fb(7)+diff(7)
      fbc(8)=fb(8)+diff(8)
      fbc(9)=fb(9)+2*rate(19)+rate(20)-rate(16)+diff(9)
C-----CALCULATE EMULSION PHASE GAS FLOW RATES (UNCORRECTED)
      fec(1)=fe(1)-0.5*rate(5)-rate(6)-rate(7)-rate(8)-rate(9)-diff(1)
      fec(2)=fe(2)+rate(1)+0.5*rate(3)-rate(4)+rate(5)-2*rate(7)
     *       +2*rate(10)-diff(2)
      fec(3)=fe(3)+rate(1)-2*rate(2)-0.5*rate(3)+rate(4)-2*rate(8)
     *       -rate(11)-diff(3)
      fec(4)=fe(4)+rate(2)+0.5*rate(3)-0.5*rate(9)-diff(4)
      fec(5)=fe(5)+rate(4)+rate(6)+2*rate(7)+0.5*rate(9)
     *       -rate(10)-diff(5)
      fec(6)=fe(6)-diff(6)
      fec(7)=fe(7)+rate(11)-diff(7)
      fec(8)=fe(8)-diff(8)
      fec(9)=fe(9)-rate(1)-0.5*rate(3)-rate(4)+2*rate(8)+rate(9)
     *       -diff(9)
C-----FORCE SULFUR SHIFT RXN TO EQUILIBRIUM
      call sshift(te,fe)
      call sshift(tb,fb)
C-----CHECK FOR NEGATIVE FLOWS (SET TO ZERO IF ANY FOUND)
      do 25 i=1,9
      if((fec(i)+fbc(i)).lt.0.0) go to 20
      if(fec(i).ge.0.0) go to 15
      fbc(i)=fbc(i)+fec(i)
      fec(i)=0.0
   15 if(fbc(i).ge.0.0) go to 25
      fec(i)=fec(i)+fbc(i)
      fbc(i)=0.0
      go to 25
   20 fec(i)=0.0
      fbc(i)=0.0
   25 continue
c
      return
      end
      subroutine sshift(t,f)
c*******************************************************************
c     SUBROUTINE SSHIFT ADJUSTS THE GAS FLOWS TO ACHIEVE
c     EQUILIBRIUM OF THE RXN   COS + H2O = H2S + CO2. THE EQUIL.
c     CONSTANT EQN CAN BE THAT DETERMINED BY PURDY (8-80), OR THAT
c     TAKEN FROM DATA PRESENTED BY KOHL AND RIESENFELD(DATA OF TERRES
c     AND WESEMANN).
c
c     t         temp, degrees rankine
c     ik        parameter which determines which equilibrium constant
c               is used;   ik=0 - purdy,   ik=1 - terres and wesemann.
c     k1        equil constant for the rxn  cos + h2o = h2s + co2
c     f(i)      flow rate of each component, lbmoles/min,
c               5=co2; 7=h2s; 8=cos; 9=h2o.
c     root      quadratic eqn solution, =lbmoles of cos produced,...
c     tk        temp, degrees kelvin
c     term1     intermediate used in soln of quadratic eqn,
c               similarly for term2 and term3.
c*******************************************************************
      dimension f(9)
      real k1
C-----TEMPORARILY SET IK=1 (TERRES AND WESEMANN EQUIL DATA)
      ik=1
      if(f(7).le.0.0.and.f(8).le.0.0) return
      tk=t*5/9
      if(ik.eq.1) go to 3
      k1=exp(3.293+3864.34/tk-0.49*alog(tk)-4.143e-4*tk
     *   +5.596e-7*tk*tk-1.558e-10*tk**3)
      go to 4
    3 k1=exp(-1.352+7881.61/t)
    4 term1=k1*(f(8)+f(9))+f(5)+f(7)
      term2=k1-1.0
      term3=sqrt(term1**2-4*term2*(k1*f(8)*f(9)-f(5)*f(7)))
      root1=(-term1+term3)/(2*term2)
      root2=(-term1-term3)/(2*term2)
      root=root1
      if(root1.gt.f(7).or.(f(8)+root1).lt.0.0) go to 5
      go to 6
    5 root=root2
    6 f(5)=f(5)-root
      f(7)=f(7)-root
      f(8)=f(8)+root
      f(9)=f(9)+root
      return
      end
      subroutine fcorr(te,tb,p,fe,fb,diff)
c*********************************************************************
c     SUBROUTINE FCORR ADJUSTS THE BUBBLE AND EMULSION PHASE GAS
c     FLOW RATES WHEN THE EMULSION FLOW DIFFERS FROM THAT CALCULATED
c     FROM BED HYDRODYNAMICS
c*********************************************************************
      dimension fe(9),fb(9),ye(9),yb(9),diff(9)
      common/blk5/qe,qb
C-----CALCULATE GAS MOLAR DENSITIES
      gemden=p/(10.73*te)
      gbmden=p/(10.73*tb)
C-----CALCULATE EMULSION AND BUBBLE PHASE TOTAL GAS FLOW
C-----RATES, BASED ON MASS BALANCE RESULTS
      fetot=0.0
      fbtot=0.0
      do 10 i=1,9
      fetot=fetot+fe(i)
   10 fbtot=fbtot+fb(i)
      qemb=fetot/gemden
      qbmb=fbtot/gbmden
C-----CALCULATE GAS MOLE FRACTIONS(UNCORRECTED)
      do 15 i=1,9
      if(fetot.gt.0.0) go to 11
      ye(i)=0.0
      go to 12
   11 ye(i)=fe(i)/fetot
   12 if(fbtot.gt.0.0) go to 13
      yb(i)=0.0
      go to 15
   13 yb(i)=fb(i)/fbtot
   15 continue
C-----CONVERT TOTAL GAS FLOWS (BASED ON BED HYDRAULICS) TO CFM
      qebh=qe*60.0
      qbbh=qb*60.0
C-----FLOW CORRECTIONS
      corr=(qemb-qebh)*gemden
      do 20 i=1,9
      fe(i)=fe(i)-corr*ye(i)
      fb(i)=fb(i)+corr*ye(i)
      diff(i)=diff(i)+corr*ye(i)
   20 continue
C-----CHECK FOR NEGATIVE FLOWS (CORRECT IF ANY FOUND)
      do 45 i=1,9
      if(fe(i).ge.0.0.and.fb(i).ge.0.0) go to 45
      if(fe(i).ge.0.0) go to 42
      fb(i)=fb(i)+fe(i)
      fe(i)=0.0
      go to 45
   42 fe(i)=fe(i)+fb(i)
      fb(i)=0.0
   45 continue
c
      return
      end
      subroutine mix(f1,f2,t1,t2,qa,f,t)
c*********************************************************************
c    MIX COMBINES GAS FLOWS F1 AND F2 WITH TEMPS T1 AND T2, AND
c    CALCULATES THE COMBINED FLOW F AND THE COMBINED TEMPERATURE T.
c    HEAT TRANSFER WITH SURROUNDINGS CAN BE ACCOUNTED FOR WITH QA.
c
c    f1,f2,f - lbmoles/min     t1,t2,t - degrees rankine
c    qa - heat addition to mixture, btu/min
c*********************************************************************
      dimension f1(9),f2(9),f(9),a(9),b(9),c(9),d(9)
      common/dat2/a,b,c,d
C-----SUM FLOW RATES
      sum1=0.0
      sum2=0.0
      do 10 i=1,9
      f(i)=f1(i)+f2(i)
      sum1=sum1+f1(i)
   10 sum2=sum2+f2(i)
      sum=sum1+sum2
C-----SUM SENSIBLE HEATS
      t=t1
      if(t1.eq.t2.and.qa.eq.0.0)return
      tref=536.7
      tref2=tref*tref
      tref3=tref2*tref
      tref4=tref3*tref
      q=qa
      do 20 I=1,9
   20 q=q + f1(I)*(a(I)*(t1-tref)+b(i)/2*(t1**2-tref2)
     1    +c(I)/3*(t1**3-tref3)+d(i)/4*(t1**4-tref4))
     1    + f2(i)*(a(i)*(t2-tref)+b(i)/2*(t2**2-tref2)
     1    +c(i)/3*(t2**3-tref3)+d(i)/4*(t2**4-tref4))
C-----ESTIMATE MIXTURE TEMPERATURE
      t=(sum1*t1+sum2*t2)/sum
C-----DETERMINE TRUE MIXTURE TEMPERATURE
      k=0
   25 qm=0.0
      k=k+1
      do 30 i=1,9
   30 qm=qm + f(i)*(a(i)*(t-tref)+b(i)/2*(t**2-tref2)
     1    +c(i)/3*(t**3-tref3)+d(i)/4*(t**4-tref4))
      if(abs(qm-q).lt.abs(0.001*q)) return
      if(k.eq.1) go to 40
      if(k.ge.20) go to 100
      x=t-(qm-q)*((t-to)/(qm-qmo))
      go to 50
   40 x=t-10.0*(qm-q)/(abs(qm-q))
   50 to=t
      qmo=qm
      t=x
      go to 25
  100 write(3,110)k
  110 format(/10x,'mix did not converge in',i3,' iterations',/)
c
      return
      end
      subroutine attrit(qc,qd,sf,time,k,dc)
c**********************************************************************
c     SUBROUTINE ATTRIT CALCULATES THE RATE OF ATTRITION
c     IN THE FLUIDIZED BED
c
c     qc      = coal rate in bed, lb/hr
c     qd      = coal rate at bed inlet, lb/hr
c     sf(10)  = inlet size distribution, wt fractions
c     dp(10)  = inlet particle sizes, ft
c     uo      = gas velocity, ft/s
c     umf     = minimum fluidization velocity, ft/s
c     time    = average residence time of solids, hr
c     k       = abrasion rate constant, 1/ft
c     dc(10)  = outlet particle sizes, ft
c**********************************************************************
      dimension sf(10),dp(10),dc(10)
      real k
      common/blk7/uo,umf,emf,ub,dbub,bvol
      common/dat5/dp
      ifail=0
      f=1.0
      term=k*(uo-umf)*3600.
      factor=(qc/qd)**(1./3.)
c
      do 100 i=1,10
      it=0
      f=f-sf(i)
C-----INITIAL GUESS, SET OUTLET SIZE = INLET SIZE
      dc(i)=dp(i)*factor
C-----CALCULATE ABRASION RATE, FT/HR
    7 it=it+1
      r=term*f*dc(i)
      if(r.lt.0.0) r=0.0
C-----CALCULATE OUTLET PARTICLE SIZE
      dcc=dp(i)*factor-r*time
      if(dcc.lt.0.0) dcc=0.0
C-----CHECK OUTLET SIZE ESTIMATE
      if(abs(dcc-dc(i)).gt.(0.01*dc(i))) go to 40
      go to 100
C-----NEW OUTLET SIZE ESTIMATE
   40 if(it.eq.1) go to 45
      denom=dc(i)-dco-dcc+dcco
      if(abs(denom).lt.1.0e-30) go to 45
      x=(dcco*(dc(i)-dco)-dco*(dcc-dcco))/denom
      go to 50
   45 x=0.5*(dc(i)+dcc)
   50 dco=dc(i)
      dcco=dcc
      dc(i)=x
      if(it.lt.10) go to 7
      ifail=1
  100 continue
      if(ifail.eq.1) write(3,105)
  105 format(/10x,'ATTRIT did not converge for all particle sizes',/)
c
      return
      end
      subroutine elut(f,t,p,ac,sb,dc,sden,dpa,abed,rtot,
     *     se,sc,dcavg,deavg,eopt)
c*********************************************************************
c     SUBROUTINE ELUT CALCULATES THE ELUTRIATION RATE
c
c     f(i) = gas flow rates, lbmoles/min.  1=O2,2=CO,3=H2,4=CH4,5=CO2,
c                                          6=N2,7=H2S,8=COS,9=H2O
c     t = temperature, R
c     p = pressure, psia
c     ac = char flow rate in bed, lb/hr
c     sb = particle size distribution in bed, wt fractions
c     dc = particle sizes, ft
c     sden = solid density, lb/ft3
c     dpa =  avg particle diameter, ft
c     abed = bed cross-sectional area, ft2
c     r(i) = elutriation rate for particle size i, lb/hr
c     rtot = total elutriation rate, lb/hr
c     sc = particle size distribution of exit char, wt fractions
c     se = particle size distribution of eluted particles, wt fractions
c     dcavg = avg particle diameter of exit char, ft
c     deavg = avg particle diameter of eluted particles, ft
c     eopt = elut option (0=no elut, 1=elutriation)
c*********************************************************************
      dimension f(9),mw(9),y(9),sb(10),dc(10),r(10),se(10),sc(10)
      common/dat1/mw
      common/dat4/g
      real mw
      integer eopt
c
      rtot=0.0
      do 2 i=1,10
      r(i)=0.0
    2 continue
      if(eopt.eq.0) go to 60
C-----CALCULATE TOTAL FLOW, MOLE FRACTIONS, AND AVG MOL. WT.
      ftot=0.0
      do 5 i=1,9
    5 ftot=ftot+f(i)
      amw=0.0
      do 10 i=1,9
      y(i)=f(i)/ftot
   10 amw=amw+y(i)*mw(i)
C-----CALCULATE ACTUAL VELOCITY (FT/S) AND
C-----MASS FLOW RATE (LB/HR-FT2) FOR GAS
      u=ftot/(abed*60.0)*359.0*(t/492.)*(14.7/p)
      fmass=ftot*amw*60.0/abed
C-----CALCULATE MINIMUM FLUIDIZATION VELOCITY
      gden=amw*p/(10.73*t)
      call vis(t,p,y,gvis)
      ar=(gden*(sden-gden)*g*dpa**3)/(gvis*gvis)
      umf=gvis/(gden*dpa)*(sqrt(637.5625+0.0651*ar)-25.25)
C-----FOR EACH PARTICLE SIZE, CALCULATE TERMINAL VELOCITY,
C-----ELUTRIATION RATE CONSTANT, AND ELUTRIATION RATE
      do 50 i=1,10
      d=dc(i)
      call vterm(t,p,y,sden,d,ut,re)
C  ---CALCULATE ELUTRIATION RATE CONSTANT, LB/(HR-FT2)
   30 e=130.0*fmass*exp(-10.4*sqrt(ut/u)*(umf/(u-umf))**0.25)
C  ---CALCULATE ELUTRIATION RATE, LB/HR
      r(i)=e*sb(i)*abed
      if(r(i).gt.(sb(i)*ac)) r(i)=sb(i)*ac
      rtot=rtot+r(i)
   50 continue
```

```
C  ---CALCULATE SIZE DISTRIBUTIONS AND AVG SIZES
  60  x=ac-rtot
      if(x.gt.0.0) go to 65
      rtot=0.0
      do 63 i=1,10
      r(i)=0.95*r(i)
  63  rtot=rtot+r(i)
      go to 60
  65  dcavg=0.0
      deavg=0.0
      if(eopt.eq.0) go to 75
      do 70 i=1,10
      se(i)=r(i)/rtot
      deavg=deavg+se(i)*dc(i)
  70  continue
  75  do 80 i=1,10
      sc(i)=(ac*sb(i)-r(i))/x
      dcavg=dcavg+sc(i)*dc(i)
  80  continue
      ac=x
c
      return
      end
      subroutine free(feed,tcoal,xp,xu,xc,sol,den,sf,hf,delhf,p,fbed,
     *     f,fd,tar,teb,top,dopt,eopt,abed,btot,s,sb,xb)
c***********************************************************************
c     SUBROUTINE FREE PERFORMS THE FREEBOARD CALCULATIONS:
c     GAS-SOLID HEAT TRANSFER AND DEVOLATILIZATION
c
c      xp - prox analysis, wt fraction   den - coal density, lb/ft3
c    feed - coal feed rate, lb/hr          sf - feed sieve analysis, wt%
c   tcoal - inlet coal temp, R             hf - height of freeboard, ft
c       p - pressure, psia              delhf - height increment, ft
c     teb - gas temp at bed exit, R         f - gas flows, lbmole/min
c      xc - char ult analysis            abed - bed area, ft2
c      xu - feed ult analysis, wt fractions
c    fbed - gas flows leaving bed, lbmol/min
c    dopt - devol option: 0=no devol, 1=devol
c    eopt - entrainment option: 0=none, 1=entrainment
c     tar - tar flow rate, lb/hr
c     top - gas temp at top of reactor, R
c    btot - solids blowover rate, lb/hr
c       s - size dist of feed after blowover, wt fractions
c      sb - size dist of blowover, wt fractions
c      xb - ult analysis of blowover, wt fractions
c***********************************************************************
      dimension w(10),dp(10),t(10),s(10),f(9),y(9),area(10),a(9),b(9),
     *    c(9),d(9),mw(9),f2(9),xp(4),xu(6),xc(6),fbed(9),fd(9),xtar(6),
     *    sb(10),fb(9),xb(6),sf(10)
      real nu,k,mw
      integer dopt,eopt
      common/dat1/mw
      common/dat2/a,b,c,d
      common/dat4/g
      common/dat5/dp
      common/dat9/xtar
      data hvap,cw/900.0,1.0/
C-----HVAP IS HEAT OF VAP OF WATER, BTU/LB.   CW IS WATER HEAT CAP,
C-----BTU/(LB R).  AVERAGE VALUES OVER THE EXPECTED TEMP/PRESSURE RANGE
C-----ARE USED.
      write(3,1)
   1  format(///41x,'FREEBOARD FLOWS AND TEMPS',//1x,'HF(ft)',3X,
     *  'COAL',5x,'GAS',6x,'TGAS(R)',3x,'PARTICLE TEMPS (R)')
      tref=536.7
      sav=delhf
      wetsav=xp(2)
      vsav=xp(3)
      coal=feed
      btot=0.0
      it=0
      iprint=0
      top=0.5*(tcoal+teb)
c
   5  tgas=top
      ht=0.0
C-----DETERMINE DEVOLATILIZATION PRODUCTS:
      call gildev(teb,coal,xp,fd,tar,vol,dopt)
      ftot=0.0
      do 2 i=1,9
      f(i)=fbed(i)+fd(i)
      ftot=ftot+f(i)
   2  continue
      if(eopt.eq.0) go to 3
C-----CALL SUBROUTINE BLOW TO CALCULATE RATE OF BLOWOVER SOLIDS
      call blow(f,tgas,p,abed,feed,xp,xu,sf,s,den,dopt,btot,xb,
     *     sb,fb,btar)
```

```
  3  coal=feed-btot
     wet=wetsav
     v=vsav
     sden=den
     sol=coal
     do 6 i=1,10
     w(i)=coal*s(i)
     area(i)=6.0*w(i)/(sden*dp(i))
  6  continue
     do 7 i=1,10
     t(i)=tcoal
  7  continue
     if(iprint.eq.1) write(3,16)ht,sol,ftot,tgas,(t(j),j=1,10)
c
C-----CALCULATIONS FOR EACH STEP IN FREEBOARD REGION:
 10  ht=ht+delhf
     if(ht.le.hf) go to 8
     delhf=delhf-(ht-hf)
     ht=hf
  8  ftot=0.0
     do 9 i=1,9
     f(i)=f(i)-fd(i)*delhf/hf
     if(f(i).lt.fbed(i)) f(i)=fbed(i)
     f2(i)=0.0
     ftot=ftot+f(i)
  9  sol=sol-fd(i)*60.0*mw(i)*delhf/hf
     sol=sol-tar*delhf/hf
     amw=0.0
     do 4 j=1,9
     y(j)=f(j)/ftot
  4  amw=amw+y(j)*mw(j)
     uo=ftot*359.0/(60.0*abed)*(tgas/492.0)*(14.7/p)
     sden=den*sol/coal
     wet=(f(9)-fbed(9))*18.02*60.0/sol
     if(wet.lt.0.0) wet=0.0
     v=coal*(vsav-vol*(1.0-wetsav)*ht/hf)*100.0/(sol*(1.0-wet))
     call vis(tgas,p,y,gvis)
     call tcon(tgas,p,y,k)
     qtot=0.0
C-----PERFORM HEAT TRANSFER CALCULATIONS FOR EACH PARTICLE SIZE CLASS
     do 15 i=1,10
     w(i)=w(i)*sol/coal
     if(w(i).le.0.0) go to 15
C-----CALCULATE TERMINAL VELOCITY AND REYNOLDS NUMBER
     x=dp(i)
     call vterm(tgas,p,y,sden,x,ut,re)
     ut=ut-uo
     if(ut.gt.0.0) go to 30
     ut=0.01
 30  time=delhf/(ut*3600.)
C-----CALCULATE PRANDTL NUMBER
     cpm=0.0
     do 13 j=1,9
 13  cpm=cpm+(a(j)+b(j)*tgas+c(j)*tgas**2+d(j)*tgas**3)*y(j)
     cpm=cpm/amw
     pr=cpm*gvis/k*60.0
C-----CALCULATE NUSSELT NUMBER (KUNII-LEVENSPIEL CORRELATION)
     nu=2.0 + 0.6*pr**(1./3.)*sqrt(re)
C-----CALCULATE HEAT TRANSFER COEFFICIENT AND RATE
C-----(H: BTU/(MIN-FT2-R),  Q: BTU/MIN )
     h=nu*k/dp(i)
     q=h*(tgas-t(i))*area(i)*time
C-----CALCULATE NEW SOLID TEMPERATURE (CS,CW:  BTU/LB.R)
```

```
      cs=0.17 + 1.1e-4*(t(i)-459.7) + (3.2e-3+3.05e-6*(t(i)-459.7))*v
      tt=t(i)+q*60.0/(w(i)*(cs*(1.0-wet)+cw*wet))
      if(tt.le.tgas) go to 14
      tt=tgas
      q=w(i)*(cs*(1.0-wet)+cw*wet)*(tt-t(i))/60.0
   14 t(i)=tt
      qtot=qtot+q
   15 continue
C-----CALCULATE GAS TEMPERATURE
      qtot=qtot+fd(9)*delhf/hf*18.02*hvap
      call mix(f,f2,tgas,tgas,qtot,f,tgas)
      if(tgas.lt.tcoal) tgas=tcoal
      if(iprint.eq.1) write(3,16)ht,sol,ftot,tgas,(t(j),j=1,10)
   16 format(1x,f5.2,f9.2,f9.4,f10.1,10f9.1)
      if(ht.lt.hf) go to 10
      delhf=sav
      if(iprint.eq.1) go to 51
C-----CHECK GAS OUTLET TEMPERATURE ESTIMATE
      it=it+1
      if(it.lt.10) go to 18
      write(3,17)
   17 format(5x,'free did not converge -- bub stopped')
      stop
   18 if(abs(tgas-teb).le.abs(0.01*teb)) go to 50
      if(it.eq.1) go to 20
      x=topo + (teb-tgaso)*((top-topo)/(tgas-tgaso))
      go to 25
   20 x=top+(teb-tgas)
   25 tgaso=tgas
      topo=top
      top=x
      go to 5
   50 iprint=1
      go to 5
C-----ADJUST COMPOSITION TO ACCOUNT FOR DRYING/DEVOLATILIZATION
   51 xc(1)=(coal*xu(1)-tar*xtar(1)-(fd(2)+fd(4)+fd(5)+fd(8))
     *       *60.0*12.01)/sol
      xc(2)=(coal*xu(2)-tar*xtar(2)-(fd(3)+2*fd(4)+fd(7)+fd(9))
     *       *60.0*2.02)/sol
      xc(3)=(coal*xu(3)-tar*xtar(3)-(2*fd(1)+fd(2)+2*fd(5)+fd(8)+fd(9))
     *       *60.0*16.00)/sol
      xc(4)=(coal*xu(4)-tar*xtar(4)-fd(6)*60.0*28.01)/sol
      xc(6)=(coal*xu(6)-tar*xtar(6))/sol
      xc(5)=1.0-(xc(1)+xc(2)+xc(3)+xc(4)+xc(6))
      do 54 i=1,6
      if(xc(i).ge.0.0) go to 54
      xc(i)=0.0
      write(3,53)i
   53 format(/10x,'in free, xc(',i1,') less than zero, set = zero',/)
   54 continue
C-----COMBINE DEVOL GASES AND TAR FROM BLOWOVER AND FREEBOARD SOLIDS
      do 52 i=1,9
      fd(i)=fd(i)+fb(i)
      f(i)=fbed(i)+fd(i)
   52 continue
      tar=tar+btar
      write(3,55)
   55 format(//t20,'HF=distance below coal inlet',8x,
     * 'COAL=coal rate, lb/hr',8x,'GAS=gas rate, lbmoles/min')
c
      return
      end
      subroutine gildev(t,coal,xp,fd,tar,vol,dopt)
c**********************************************************************
c     SUBROUTINE GILDEV CALCULATES THE DEVOLATILIZATION
c     PRODUCT FLOW RATES.  USED ARE: FRIEDMAN'S DATA FOR CO,CO2,
c     CH4,H2, AND TAR; GILMAN'S H2S AND COS DATA;
c     AND KAU'S TOTAL WEIGHT LOSS CORRELATION.
c
c     avgmw =  average mol wt of devolatilized gases
c     char  =  solid flow rate after devolatilization
c     dafwl =  dry-ash-free weight loss (wt fraction)
c     dopt  =  devol option: 0=only drying, 1=drying and devol.
c     fd(i) =  flow rate of devol gases, lbmoles/min
c     fdtot =  total flow rate of devolalitilzed gases
c     ftar  =  fraction of wdevol that is tar.
c     t     =  temperature, rankine
c     tk    =  temperature, kelvin
c     tar   =  amount of tar produced, lbs/hr
c     coal  =  feed rate of coal, lbs/hr
c     wdevol=  mass of coal devolalitized(excluding moisture), lbs/hr
c     xp    =  proximate analysis (wt fractions)
c     mw    =  mol weights of gases, lbs/lbmole
c     yd    =  mole fractions of devol gases
c***********************************************************************
      dimension xp(4),fd(9),yd(9),mw(9)
      integer dopt
      real mw
      common/dat1/mw
      data yd/0.0,0.194,0.279,0.372,0.155,0.0,0.002,0.00014,0.0/
      vol=0.0
      if(dopt.eq.0) go to 160
      ftar=0.34
      tk=(5./9.)*t
C-----CALCULATE FLOW RATES OF DEVOLALITIZATION PRODUCTS
      dafwl=1.05-7.15e-3*tk+1.61e-5*tk*tk-1.37e-8*tk**3+4.04e-12*tk**4
      wdevol=coal*dafwl*(1.-xp(2)-xp(4))
      vol=wdevol/(coal*(1.0-xp(2)))
      avgmw=0.0
      do 100 i=2,8
      avgmw=avgmw+mw(i)*yd(i)
 100  continue
      tar=ftar*wdevol
      fdtot=(wdevol-tar)/(avgmw*60.0)
      do 150 i=1,8
      fd(i)=fdtot*yd(i)
 150  continue
 160  fd(9)=xp(2)*coal/(60.*mw(9))
c
      return
      end
      subroutine blow(f,t,p,abed,coal,xp,xu,sf,s,sden,dopt,btot,xb,
     *       sb,fb,tar)
c*********************************************************************
c     SUBROUTINE BLOW CALCULATES THE FLOW RATE AND COMPOSITION OF
c     FINES IN THE COAL FEED STREAM THAT ARE IMMEDIATELY BLOWN
c     OUT OF THE REACTOR
c
c     f(9)   gas flow rates, lbmoles/min
c     t      gas temperature, rankine
c     p      pressure, psia
c     abed   bed cross-sectional area, ft2
c     coal   coal feed rate, lb/hr
c     xp(4)  feed coal proximate analysis, wt fractions
c            (1=fc, 2=moist, 3=vm, 4=ash)
c     xu(6)  ult analysis of feed, wt fractions (c,h,o,n,s,ash)
c     sf(10) feed coal size distribution, wt fractions
c     s(10)  size distribution after blowover, wt fractions
c     sden   feed coal density, lb/ft3
c     dopt   devol option, 0=no devol, 1=devol
c     btot   total blowover rate, lb/hr
c     xb(6)  ult analysis of blowover, wt fractions (c,h,o,n,s,ash)
c     sb(10) size distribution of blowover, wt fractions
c     fb(9)  gas flows due to devol of blowover, lbmoles/min
c     tar    tar evolved from blowover, lb/hr
c*********************************************************************
      dimension f(9),s(10),dp(10),y(9),b(10),xp(4),fb(9),xtar(6),
     *     sf(10),sb(10),xb(6),xu(6)
      common/dat5/dp
      common/dat9/xtar
      integer dopt
C-----CALCULATE TOTAL GAS FLOW, MOLE FRACTIONS, AND AVG MOL WT
      ftot=0.0
      do 10 i=1,9
  10  ftot=ftot+f(i)
      do 20 i=1,9
      y(i)=f(i)/ftot
  20  continue
C-----CALCULATE GAS VELOCITY
      uo=ftot*359.0/(60.0*abed)*(t/492.)*(14.7/p)
C-----DETERMINE BLOWOVER RATES
      btot=0.0
      do 100 i=1,10
      d=dp(i)
      call vterm(t,p,y,sden,d,ut,re)
      b(i)=0.0
      if(ut.gt.uo) go to 100
      b(i)=coal*sf(i)
      btot=btot+b(i)
 100  continue
      if(btot.le.0.0) return
C-----CALCULATE ADJUSTED COAL FEED, AND SIZE DISTRIBUTIONS
      x=coal-btot
      do 150 i=1,10
      sb(i)=b(i)/btot
      s(i)=(coal*sf(i)-b(i))/x
 150  continue
C-----DETERMINE DEVOL PRODUCTS FROM BLOWNOVER SOLIDS
      call gildev(t,btot,xp,fb,tar,vol,dopt)
C-----CALCULATE EXIT COMPOSITION OF BLOWOVER SOLIDS
      x=btot*(1.0-xp(2)-vol*(1.0-xp(2)))
      xb(1)=(btot*xu(1)-tar*xtar(1)-(fb(2)+fb(4)+fb(5)+fb(8))
     *     *60.0*12.01)/x
      xb(2)=(btot*xu(2)-tar*xtar(2)-(fb(3)+2*fb(4)+fb(7)+fb(9))
     *      *60.0*2.02)/x
      xb(3)=(btot*xu(3)-tar*xtar(3)-(2*fb(1)+fb(2)+2*fb(5)+fb(8)+fb(9))
     *      *60.0*16.00)/x
      xb(4)=(btot*xu(4)-tar*xtar(4)-fb(6)*60.0*28.01)/x
      xb(6)=(btot*xu(6)-tar*xtar(6))/x
      xb(5)=1.0-xb(1)-xb(2)-xb(3)-xb(4)-xb(6)
c
      return
      end
      subroutine vterm(t,p,y,sden,d,ut,re)
c**********************************************************************
c     SUBROUTINE VTERM CALCULATES THE TERMINAL VELOCITY OF
c     A GIVEN PARTICLE IN A SPECIFIED GAS ENVIRONMENT
c
c     t     gas temperature, rankine
c     p     pressure, psia
c     y(i)  gas mole fractions  (o2,co,h2,ch4,co2,n2,h2s,cos,h2o)
c     sden  particle density, lb/ft3
c     d     particle diameter, ft
c     ut    terminal velocity, ft/s
c**********************************************************************
      dimension y(9),mw(9)
      real mw
      common/dat1/mw
      common/dat4/g
C-----DETERMINE GAS PROPERTIES
      amw=0.0
      do 10 i=1,9
  10  amw=amw+y(i)*mw(i)
      call vis(t,p,y,gvis)
      gden=amw*p/(10.73*t)
C-----ASSUME 0.4<RE<500
      ut=d*((4*((sden-gden)*g)**2)/(225*gden*gvis))**(1./3.)
      re=d*gden*ut/gvis
      if(re.ge.0.4.and.re.le.500) return
C  ---ASSUME RE>500
      ut=sqrt(3.1*g*(sden-gden)*d/gden)
      re=d*gden*ut/gvis
      if(re.gt.500) return
C  ---ASSUME RE<0.4
      ut=g*(sden-gden)*d*d/(18.0*gvis)
      re=d*gden*ut/gvis
c
      return
      end
      subroutine ebal(coal,char,parts,fin,fpn2,fout,t1,t2,t3,
     *    t4,t5,t6,vm,pdiff)
c**********************************************************************
c     SUBROUTINE EBAL PERFORMS AN ENERGY BALANCE AROUND THE REACTOR
c
c  Temperatures: (all Rankine)                     Flows:
c    t1 = coal feed       t4 = char out            coal,char,parts - lb/hr
c    t2 = gas feed        t5 = gases out           fin,fpn2,fout-lbmol/min
c    t3 = purge n2        t6 = particulates out
c
c          vm = wt % volatile matter in feed, dry basis
c     a,b,c,d = constants in gas heat capacity equation
c         hin = sensible heat in (total in), btu/hr
c        hout = sensible heat out, btu/hr
c        hrxn = heat of rxn, btu/hr (- for exothermic; + for endo)
c       pdiff = % difference between energy in and energy out
c*********************************************************************
      dimension a(9),b(9),c(9),d(9),fout(9),fin(9)
      common/dat2/a,b,c,d
c
      tref=536.7
      tref2=tref*tref
      tref3=tref2*tref
      tref4=tref3*tref
C-----CALCULATE MEAN HEAT CAPACITIES FOR SOLID STREAMS [BTU/(LB R)]
      CPT1=0.17+1.1e-4*(t1-459.7)+(3.2e-3+3.05e-6*(t1-459.7))*vm
      cpt4=0.17+1.1e-4*(t4-459.7)
      cpt6=0.17+1.1e-4*(t6-459.7)
C-----CALCULATE HIN
      hin=0.0
      do 30 i=1,9
  30  hin=hin + fin(i)*(a(i)*(t2-tref)+b(i)/2*(t2**2-tref2)
     1    +c(i)/3*(t2**3-tref3)+d(i)/4*(t2**4-tref4))*60.0
      hin=hin + fpn2*(a(6)*(t3-tref)+b(6)/2*(t3**2-tref2)
     1    +c(6)/3*(t3**3-tref3)+d(6)/4*(t3**4-tref4))*60.0
      hin=hin + coal*cpt1*(t1-tref)
C-----CALCULATE HOUT
      hout=0.0
      do 40 i=2,9
  40  hout=hout + fout(i)*(a(i)*(t5-tref)+b(i)/2*(t5**2-tref2)
     1     +c(i)/3*(t5**3-tref3)+d(i)/4*(t5**4-tref4))*60.0
      hout=hout + char*cpt4*(t4-tref) + parts*cpt6*(t6-tref)
C-----CALCULATE HRXN
      call htrxn(fin,fout,hrxn)
C-----CHECK ENERGY BALANCE
      pdiff=(hout+hrxn-hin)/hout*100.0
c
      return
      end
      subroutine htrxn(fr,fp,hrxn)
c***********************************************************************
c     HTRXN CALCULATES THE STANDARD HEAT OF REACTION AT 25 DEG C,
c     GIVEN THE REACTANTS AND PRODUCTS
c
c     fr: reactants, lbmoles/min
c     fp: products, lbmoles/min
c     hrxn: heat of reaction, btu/hr
c           negative for exothermic rxn
c           positive for endothermic rxn
c***********************************************************************
      dimension fr(9),fp(9),hf(9)
      common/dat7/hf
c
      hrxn=0.0
      do 20 i=1,9
   20 hrxn=hrxn + (fp(i)-fr(i))*hf(i)*60.0
c
      return
      end
      subroutine vis(t,psia,ycomp,gvis)
c *************************************************************
c        SUBROUTINE VIS CALCULATES THE VISCOSITY OF
c        GAS MIXTURES
c
c             t = temperature, rankine
c             psia = pressure , psia
c             ycomp = gas mole fractions
c             gvis = mixture viscosity, lb/(ft-s)
c
c        gas viscosity is calculated from the polynomial equations
c        suggested by rohsenow and hartnett in their 'handbook of
c        heat transfer,' mcgraw-hill, new york(1973), pp 2-80.
c        mixture gas viscosity calculated using wilke parameters
c        suggested by reid, prausnitz, and sherwood,'properties
c        of gases and liquids,' mcgraw-hill, new york(1977).
c *************************************************************
         dimension v(9),phi(9,9),tc(9),vc(9),zc(9),ycomp(9),mw(9)
         real mw
         common/dat1/mw
         common/dat6/tc,vc,zc
         p=psia/14.696
         tk=(5.0/9.0)*t
         t2=tk**2
         t3=tk**3
         t4=tk**4
         t5=tk**5
C---CALCULATE THE INDIVIDUAL GAS VISCOSITIES
C  ---VISCOSITY OF OXYGEN
         if(ycomp(1).lt.0.001) go to 90
         v(1)=-9.24353+9.41787E-1*tk-9.02673E-4*t2+5.91612E-7*t3
     *        -14.4572E-11*t4
C  ---VISCOSITY OF CARBON DIOXIDE
 90      if(ycomp(5).lt.0.001) go to 100
         v(5)=-5.4384+5.9427E-1*tk-2.5895E-4*t2+0.64557E-7*t3
C  ---VISCOSITY OF HYDROGEN SULFIDE
 100     if(ycomp(7).lt.0.001) go to 110
         v(7)=11.63+0.41*tk
C  ---VISCOSITY OF CARBONYL SULFIDE
 110     if(ycomp(8).lt.0.001) go to 120
         v(8)=0.0
C  ---VISCOSITY OF HYDROGEN
 120     if(ycomp(3).lt.0.001) go to 140
         v(3)=2.105+4.774E-1*tk-9.9784E-4*t2+16.1027E-7*t3
     *        -128.024E-11*t4+38.164E-14*t5
C  ---VISCOSITY OF CARBON MONOXIDE
 140     if(ycomp(2).lt.0.001) go to 150
         v(2)=23.64+5.87648E-1*tk-2.73351E-4*t2+0.655858E-7*t3
C  ---VISCOSITY OF NITROGEN
 150     if(ycomp(6).lt.0.001) go to 160
         v(6)=5.2239+7.2345E-1*tk-5.8131E-4*t2+3.2167E-7*t3
     *        -7.0193E-11*t4
C  ---VISCOSITY OF METHANE
 160     if(ycomp(4).lt.0.001) go to 170
         v(4)=1.08617+4.08666E-1*tk-1.381078E-4*t2
C  ---VISCOSITY OF WATER
 170     if(ycomp(9).lt.0.001) go to 200
         v(9)=9.65+2.9347E-1*tk+0.92109E-4*t2-0.41666E-7*t3
C---CALCULATE THE WILKE PARAMETERS
 200     vistot=0.0
         do 210 i=1,9
         if(ycomp(i).lt.0.001) go to 210
         if(v(i).le.0.0) go to 210
      do 205 j=1,9
      if(i.eq.j) phi(i,j)=1.0
      if(i.eq.j) go to 205
      if(ycomp(j).lt.0.001) go to 205
      if(v(j).le.0.0) go to 205
      r1=(v(i)/v(j))**0.5
      r2=(mw(j)/mw(i))**0.25
      r3=(1+r1*r2)**2.0
      r4=(8.0*(1+mw(i)/mw(j)))**0.5
      phi(i,j)=r3/r4
205   continue
210   continue
C---CALCULATE MIXTURE VISCOSITY
      b=0.0
      do 300 i=1,9
      if(ycomp(i).eq.0.0) go to 300
      b2=0.0
      b1=ycomp(i)*v(i)
      do 310 j=1,9
      if(ycomp(j).eq.0.0) go to 310
      b2=b2+ycomp(j)*phi(i,j)
310   continue
      if(b2.eq.0.0) go to 300
      b=b+(b1/b2)
300   continue
      vismix=b
C---CALCULATE PRESSURE CORRECTION:
350   tcm=0.0
      vcm=0.0
      zcm=0.0
      xmwt=0.0
      do 400 i=1,9
      tcm=tcm+tc(i)*ycomp(i)
      vcm=vcm+vc(i)*ycomp(i)
      zcm=zcm+zc(i)*ycomp(i)
      xmwt=xmwt+mw(i)*ycomp(i)
400   continue
      pcm=zcm*tcm*82.054/vcm
      rhocm=pcm/(zcm*82.054*tcm)
      em=(tcm**(1.0/6.0))/((xmwt**0.5)*(pcm**(2.0/3.0)))
      rhom=p/(82.054*tk)
      rhored=rhom/rhocm
      e1=exp(1.439*rhored)
      e2=exp(-1.111*(rhored**1.858))
      e3=(e1-e2)*1.08/em
      gvis=(vismix+e3)*6.722e-8
c
      return
      end
      SUBROUTINE GDIFF(T,PSIA,DGAB)
c ***************************************************************
c   SUBROUTINE GDIFF CALCULATES BINARY GAS DIFFUSIVITIES
c
c    dgab: ft**2/s.   t! temp, rankine    psia:  pressure, psia
c ***************************************************************
  real mw,mwab
      dimension sigma(9),ek(9),dipole(9),vb(9),v(9),tb(9),mw(9),
     1  dgab(9,9)
      common/dat1/mw
      data sigma/3.467,3.69,2.827,3.758,3.941,3.798,3.623,4.13,2.641/
      data ek/106.7,91.7,59.7,148.6,195.2,71.4,301.1,336.0,809.1/
      data dipole/0.0,0.1,0.0,0.0,0.0,0.0,0.9,0.7,1.8/
      data vb/25.6,30.7,14.3,37.7,34.0,31.2,32.9,51.5,18.9/
      data v/16.6,18.9,7.07,24.42,26.9,17.9,20.96,38.98,12.7/
      data tb/90.2,81.7,20.4,111.7,194.7,77.4,212.8,222.9,373.2/
      data a,b,c,d,e,f,g,h/1.06036,0.15610,0.19300,0.47635,1.03587,
     1      1.52996,1.76474,3.89411/
c
      tk=(5.0/9.0)*t
      p=psia/14.696
      n=9
c
      do 200 i=1,n
      ii=i
      do 200 j=ii,n
      sigab=sqrt(sigma(i)*sigma(j))
      eab=sqrt(ek(i)*ek(j))
      mwab=sqrt((1.0/mw(i))+(1.0/mw(j)))
      delta1=1.94e-3*dipole(i)*dipole(i)/(vb(i)*tb(i))
      delta2=1.94e-3*dipole(j)*dipole(j)/(vb(j)*tb(j))
      deltab=sqrt(delta1*delta2)
      tprime=tk/eab
      omega=a/(tprime**b)+c/(exp(d*tprime))+e/(exp(f*tprime))
      if(tprime.lt.22.6) omega=omega+g/(exp(h*tprime))
      omega=omega+0.19*(deltab*deltab)/tprime
      dgab(i,j)=0.001858*(tk**1.5)*mwab/(p*(sigab*sigab)*omega)
      dgab(i,j)=dgab(i,j)*1.0764e-3
 200  dgab(j,i)=dgab(i,j)
c
      return
      end
      subroutine tcon(t,psia,comp,k)
c*****************************************************************
c       SUBROUTINE TCON CALCULATES THERMAL CONDUCTIVITIES
c       FOR GAS MIXTURES
c
c          t - temp, rankine        psia - pressure, psia
c       comp - gas mole fractions  k - gas thermal conductivity,
c                                      btu/(min-ft-R)
c******************************************************************
      real k,mw
      dimension c0(9),c(9),c1(9),tc(9),vc(9),zc(9),mw(9),
     *          gtcon(9),comp(9)
      common/dat1/mw
      common/dat6/tc,vc,zc
      data c0/0.0,0.586,3.76,0.0,4.61,0.5815,0.0,0.0,0.0/
      data c/0.0,218.0,166.0,0.0,6212.0,208.8,0.0,0.0,0.0/
      data c1/0.0,-7.8,-10.0,0.0,-10.0,-12.0,0.0,0.0,0.0/
      tk=t/1.8
      p=psia/14.696
C-------CALCULATE INDIVIDUAL GAS THERMAL CONDUCTIVITIES
C       THERMAL CONDUCTIVITY OF OXYGEN
      if(comp(1).lt.0.001) go to 10
      gtcon(1)=8.71e-3 + 3.22e-5*tk
C       THERMAL CONDUCTIVITY OF CARBON MONOXIDE
 10   if(comp(2).lt.0.001) go to 20
      a1=c0(2)*sqrt(tk)
      a2=(c(2)/tk)*10.0**(c1(2)/tk)
      gtcon(2)=(a1/(1.0+a2))*242.0e-5
C       THERMAL CONDUCTIVITY OF HYDROGEN
 20   if(comp(3).lt.0.001) go to 30
      a1=c0(3)*sqrt(tk)
      a2=(c(3)/tk)*10.0**(c1(3)/tk)
      gtcon(3)=(a1/(1.0+a2))*242.0e-5
C       THERMAL CONDUCTIVITY OF METHANE
 30   if(comp(4).lt.0.001) go to 40
      gtcon(4)=(0.029954*tk-0.864905)*242.0e-5
C       THERMAL CONDUCTIVITY OF CARBON DIOXIDE
 40   if(comp(5).lt.0.001) go to 50
      a1=c0(5)*sqrt(tk)
      a2=(c(5)/tk)*10.0**(c1(5)/tk)
      gtcon(5)=(a1/(1+a2))*242.0e-5
C       THERMAL CONDUCTIVITY OF NITROGEN
 50   if(comp(6).lt.0.001) go to 60
      a1=c0(6)*sqrt(tk)
      a2=(c(6)/tk)*10.0**(c1(6)/tk)
      gtcon(6)=(a1/(1.0+a2))*242.0e-5
C       THERMAL CONDUCTIVITY OF HYDROGEN SULFIDE
 60   if(comp(7).lt.0.001) go to 70
      gtcon(7)=(0.01486*tk-0.98946)*242.0e-5
C       THERMAL CONDUCTIVITY OF CARBONYL SULFIDE
 70   if(comp(8).lt.0.001) go to 80
      gtcon(8)=0.0
C       THERMAL CONDUCTIVITY OF WATER
 80   if(comp(9).lt.0.001) go to 90
      gtcon(9)=-1.12e-2 + 6.26e-5*tk
C-------CALCULATE THE MIXTURE THERMAL CONDUCTIVITY AT LOW PRESSURE
 90   b1=0.0
      b2=0.0
      do 100 i=1,9
      b1=b1+comp(i)*gtcon(i)*mw(i)**(1.0/3.0)
      b2=b2+comp(i)*mw(i)**(1.0/3.0)
 100  continue
      tcmix=b1/b2
```

```
C-------PRESSURE CORRECTION
      xmwg=0.0
      tcm=0.0
      zcm=0.0
      vcm=0.0
      do 110 i=1,9
      tcm=tcm+comp(i)*tc(i)
      zcm=zcm+comp(i)*zc(i)
      vcm=vcm+comp(i)*vc(i)
      xmwg=xmwg+comp(i)*mw(i)
  110 continue
      r=82.0567
      pcm=zcm*r*tcm/vcm
      rhocm=1/vcm
      rhom=p/(r*tk)
      rhored=rhom/rhocm
      gamma=(tcm**(1.0/6.0))*sqrt(xmwg)/pcm**(2.0/3.0)
      if(rhored.gt.0.5) go to 120
      k=tcmix+(14.0e-8/(gamma*zcm**5.0))*(exp(0.535*rhored)-1.0)*242.0
      go to 150
  120 if(rhored.gt.2.0) go to 130
      k=tcmix+(13.1e-8/(gamma*zcm**5.0))*(exp(0.67*rhored)-1.069)*242.0
      go to 150
  130 k=tcmix+(2.976e-8/(gamma*zcm**5.0))*(exp(1.155*rhored)+2.016)*242.0
  150 k=k/60.0
c
      return
      end
```

APPENDIX C
QUALITY CONTROL EVALUATION REPORT

The major emphasis of this report is the description and verification of a mathematical model of the fluidized-bed gasifier. The primary justification for this work was to develop a model with the objective of using it to draw conclusions regarding environmental effects, and to make predictions and generalizations for operating conditions not studied experimentally. Since the results of the research described in this report depend primarily on experimental data, the main emphasis of the quality assurance program for this project is focused on the quality of the experimental data. The quality assurance effort was therefore concentrated in three major areas:

1. Operation of the pilot plant facility at a well defined steady state so that the condition under which samples were taken was well defined and reproducible.

2. The development of reliable sampling and sample preservation techniques.

3. The development of accurate chemical analysis methods and the use of statistical methods for reporting and evaluating analytical results.

STEADY STATE OPERATION

When a run is performed on the gasifier, the acid gas removal system, or the two in combination, selected process variables (temperatures, pressures, flow rates, etc., in various parts of the system) are monitored continuously from the control room. The data acquisition system continuously monitors and stores the data from 96 process variable sensors on a disk for the permanent record of a run. When a clear steady-state has been attained, replicate samples of the various gas and condensed phase process and effluent streams are drawn and analyzed.

Figures 55 through 59 show plots of some of the important process variables from the data acquisition system and are tracings of computer plots made from the saved data file. The long tic marks shown on the plots indicate the times at which gas samples were taken for analysis.

Figures 55 and 56 show plots of the revolutions per minute of the coal feed screw, which is directly proportional to the coal feed rate, and the steam feed rate to the reactor in pounds per hour. These are independently controlled input streams. The speed of the coal feed screw is essentially constant, while the steam feed rate shows fluctuations typical of metering and control of a saturated steam flow. These fluctuations are effectively damped out by the large volume of the steam superheater before entering the reactor.

Figures 57 through 59 are plots of reactor pressure, temperature, and dry make-gas flow. The make-gas flow rate shows fluctuations due to the temperature and pressure controllers, but is essentially constant during the steady state portion of the run when samples were taken. The make-gas flow rate is the most sensitive test of a good steady state operation.

MASS BALANCES

The most useful and critical test of the quality of the experimental results, is good mass balance closures, both on total mass and on all elements of interest.

Following the run, results from on-line process measurements and off-line chemical analyses are read in as data to a computer program, which executes material and energy balance calculations, and prints out a run summary. A representative output from the gasifier data analysis program is shown in Table 24. The data are from run GO-84, one of the runs using the New Mexico subbituminous coal used in the model development. The balance closures shown in this table are typical of those attained in recent runs -- balances on total mass and major elements typically close to within 5%, and balances on sulfur to within 10%. Closures on trace elements are predictably much less satisfactory; a substantial effort to improve the accuracy and precision of trace element sampling and analysis methods is part of the current project research program.

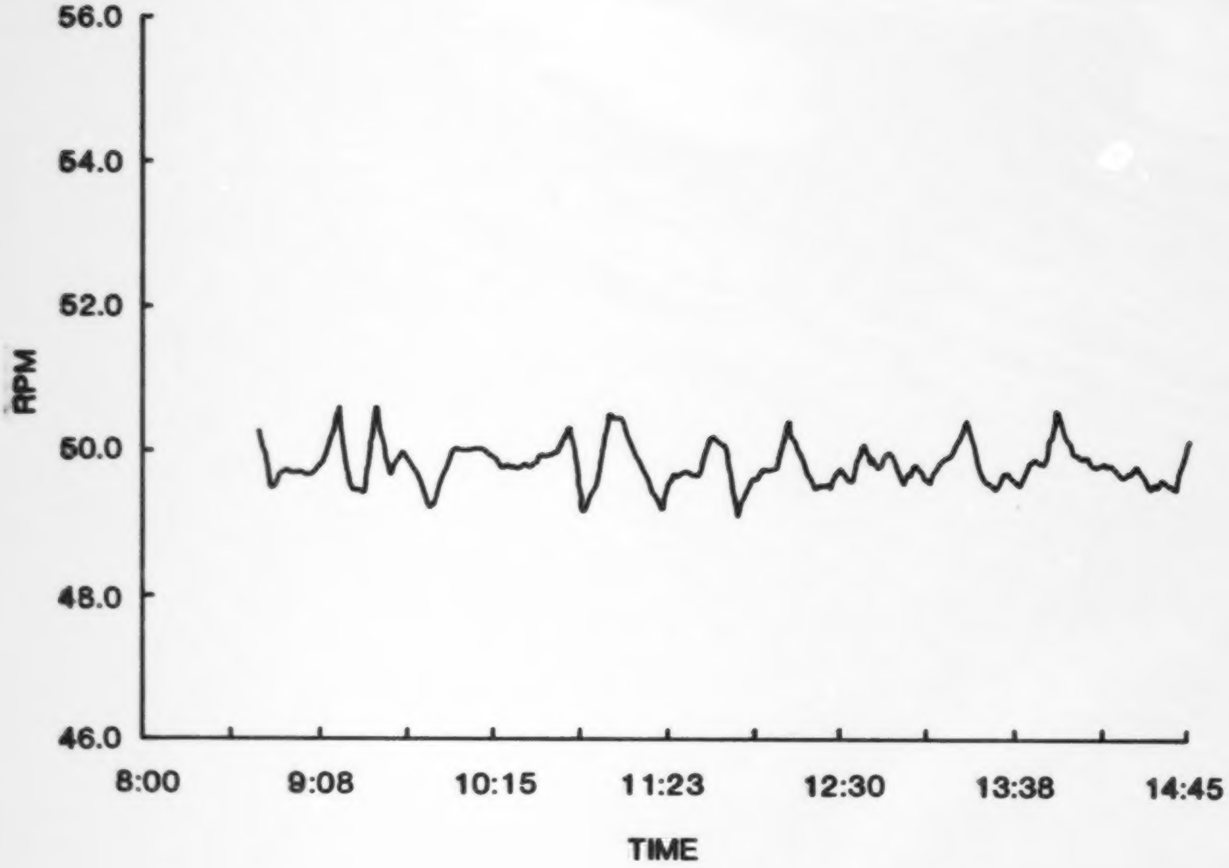

Figure 55

Coal Feed Screw Rotation

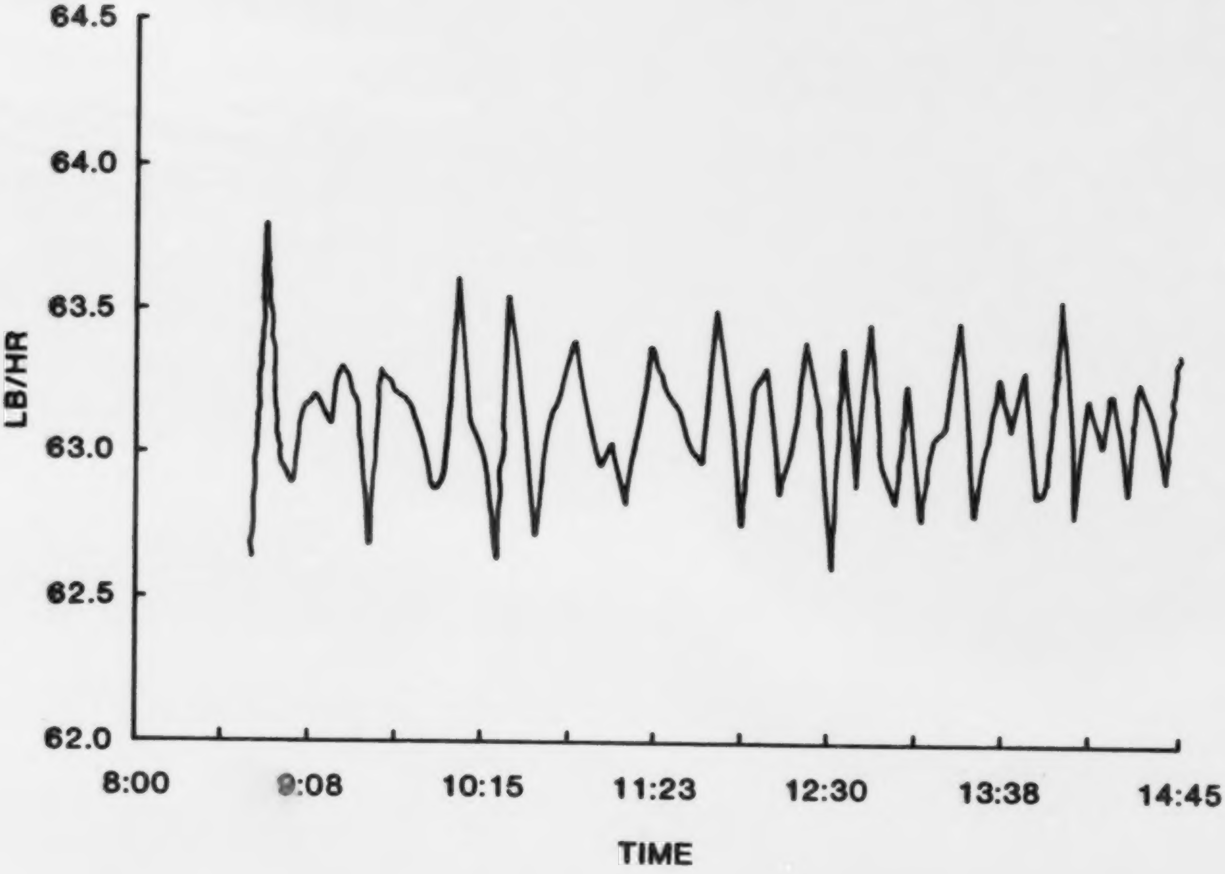

Figure 56

Steam Flow Rate to Gasifier

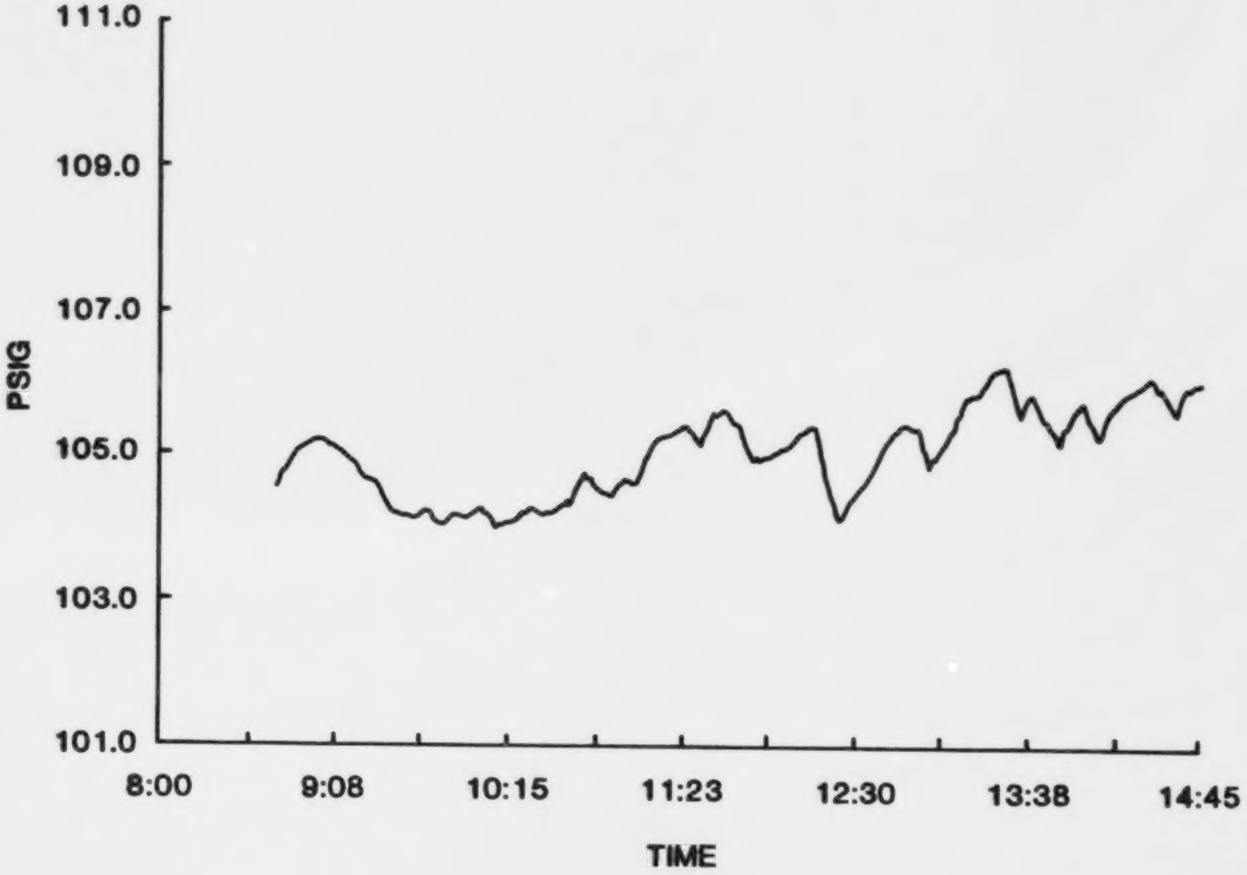

Figure 57

Gasifier Pressure

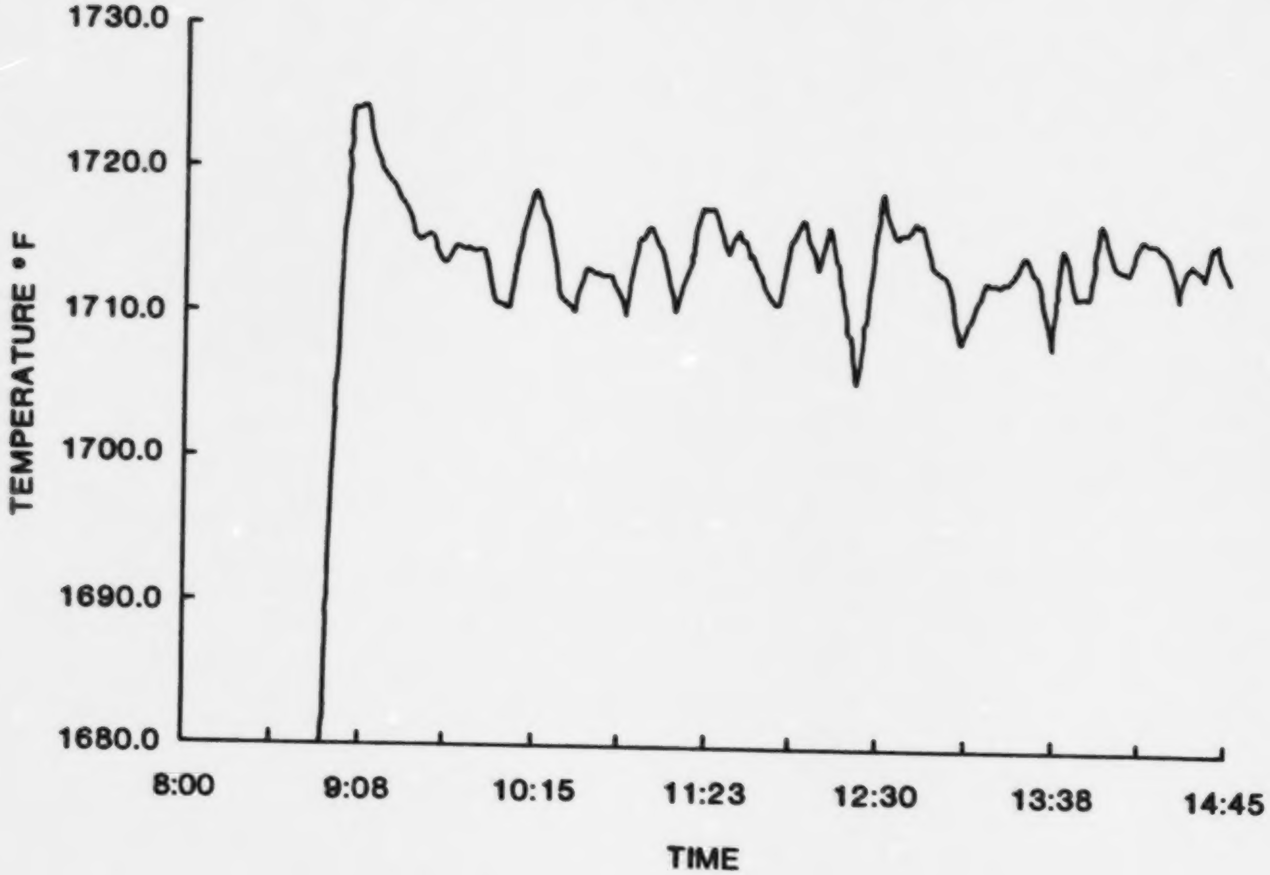

Figure 58

Gasifier Bed Temperature at 10-inch Level

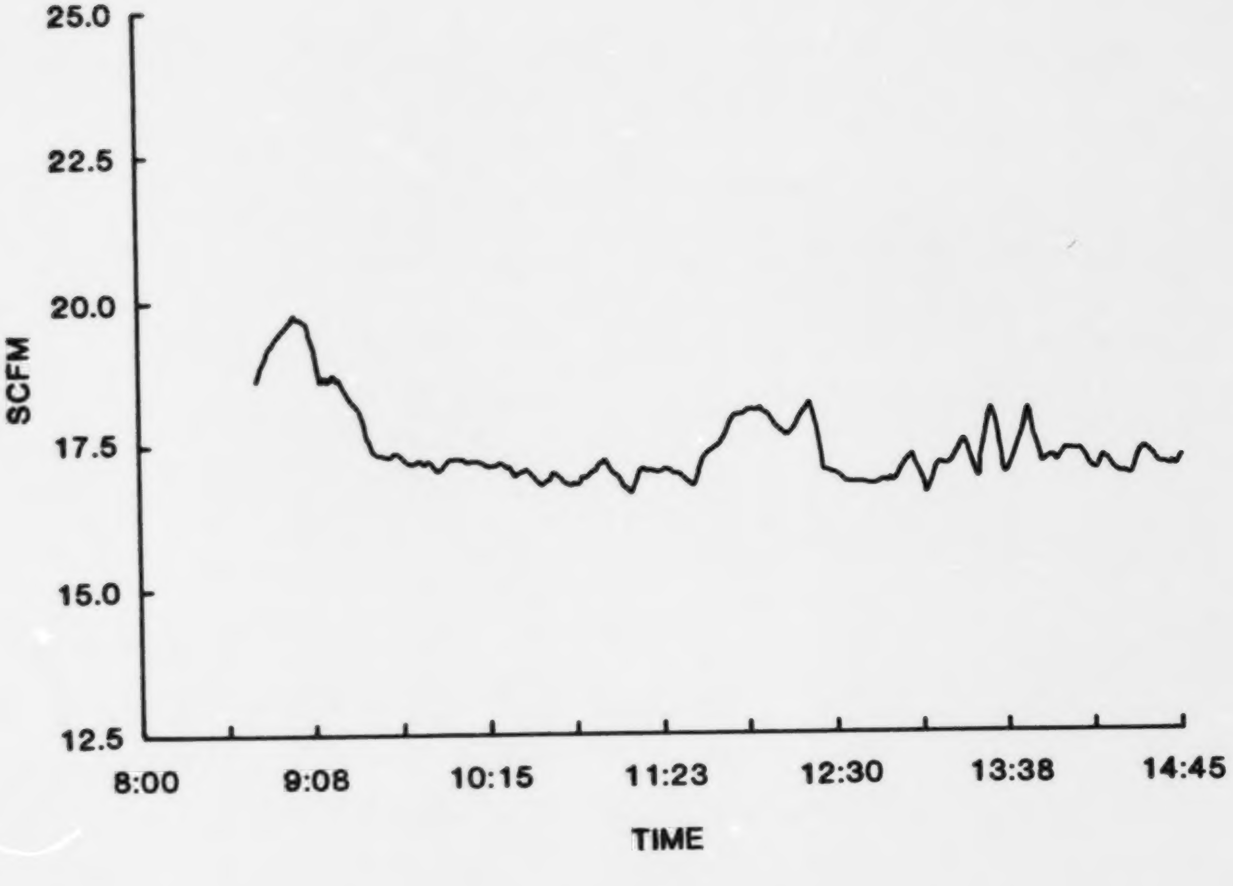

Figure 59

Gasifier Make Gas Flow Rate

Table 24
NCSU DEPARTMENT OF CHEMICAL ENGINEERING
FLUIDIZED BED GASIFICATION REACTOR
GO-84 3/3/82 13:00-14:30

REACTOR SPECIFICATIONS

Pressure	829.8 kPa (105.7 psig)
Temperature	924.9 C (1696.8 F)
Bed Height	0.97 m (38.0 in)
Bed Diameter	0.15 m (6.0 in)
Estimated Bed Voidage	0.87
Bed Expansion Factor	4.94
Leak Rate	0.016 SCMM (0.55 SCFM)

SOLID FEED PROPERTIES

New Mexico Subbituminous Coal

Particle Density	1.323 g/cc (82.6 lb/cf)
Settled Bed Density	0.830 g/cc (51.8 lb/cf)
Avg Particle Diameter	0.678 mm (0.0267 in)

Proximate Analysis	
Fixed Carbon	0.3262
Vol. Matter	0.3011
Moisture	0.0924
Ash	0.2803

Ultimate Analysis	
C	0.4833
H	0.0403
O	0.1760
N	0.0119
S	0.0082
Ash	0.2803

FEED RATES

Coal	21.70 kg/hr (47.83 lb/hr)
Steam	28.62 kg/hr (63.09 lb/hr)
Oxygen	5.26 kg/hr (11.61 lb/hr)
	0.061 SCMM (2.17 SCFM)
Nitrogen	1.76 kg/hr (3.89 lb/hr)
	0.024 SCMM (0.83 SCFM)
Purge N_2	4.09 kg/hr (9.01 lb/hr)
	0.055 SCMM (1.93 SCFM)

Molar S/C Ratio	1.82
Molar O_2/C Ratio	0.19
Molar N_2/O_2 Ratio	0.38
Coal Feed Temp	93.3 C (200.0 F)
Gas Feed Temp	530.7 C (987.3 F)
Gas Velocity	0.33 m/s (1.09 ft/s)
Min Fluid Velocity	0.03 m/s (0.11 ft/s)
Gas Vel/Min Fluid Vel	10.06

Table 24 Continued
REACTOR OUTPUT

Gas Flow Rate (wet)	2.583 kmol/hr (5.694 lbmol/hr)
	0.965 SCMM (34.07 SCFM)
Gas Flow Rate (dry)	1.220 kmol/hr (2.689 lbmol/hr)
	0.456 SCMM (16.09 SCFM)
Char Removal Rate	4.91 kg/hr (10.82 lb/hr)
Cyclone Dust Rate	2.14 kg/hr (4.71 lb/hr)
Tar Rate	1.66 kg/hr (3.67 lb/hr)
Bed DP over 20 in.	0.844 kPa (0.122 psi)
Solid Holdup	2.96 kg (6.52 lb)

SOLID EFFLUENTS

	Char	Dust	Tar
C	0.1596	0.4126	0.8000
H	0.0063	0.0091	0.1000
O	0.0042	0.0232	0.0800
N	0.0059	0.0053	0.0050
S	0.0040	0.0036	0.0050
Ash	0.8200	0.5462	0.0100

CONVERSIONS

Carbon	71.8 %
Sulfur	75.6 %

RESIDENCE TIMES

Gas	2.91 s
Solid	8.18 min

ELEMENTAL MATERIAL BALANCES : FLOWS IN KG/HR

	Mass	C	H	O	N	S
Input						
Coal	21.7	10.49	0.87	3.82	0.26	0.178
Gases	39.7	0.00	3.21	30.67	5.85	0.000
Total	61.4	10.49	4.08	34.49	6.11	0.178
Output						
Char	4.9	0.78	0.03	0.02	0.03	0.019
Dust	2.1	0.88	0.02	0.05	0.01	0.008
Tar	1.7	1.33	0.17	0.13	0.01	0.008
Gases	52.4	7.53	4.00	34.81	5.91	0.134
Water	0.2	0.00	0.03	0.00	0.16	0.026
Total	61.3	10.53	4.24	35.01	6.11	0.196
Recovery	99.8%	100.4%	103.9%	101.5%	100.1%	110.0%

Table 24 Continued
GAS ANALYSIS

	% Wet	% Dry	kg/hr	lb/hr	g/kg Feed
H_2O	52.7700	0.0000	2.46E+01	5.41E+01	1.13E+03
CO	7.4353	15.7427	5.38E+00	1.19E+01	2.48E+02
H_2	15.7020	33.2457	8.19E-01	1.81E+00	3.78E+01
CH_4	3.0436	6.4443	1.26E+00	2.78E+00	5.81E+01
CO_2	12.0148	25.4390	1.37E+01	3.01E+01	6.29E+02
N_2	8.1633	17.2842	5.91E+00	1.30E+01	2.72E+02
H_2S	0.1565	0.3314	1.38E-01	3.04E-01	6.35E+00
COS	0.0034	0.0072	5.28E-03	1.16E-02	2.43E-01
CS_2	0.0000	0.0001	9.29E-05	2.05E-04	4.28E-03
MeSH	0.0013	0.0027	1.58E-03	3.49E-03	7.30E-02
Thiophene	0.0011	0.0023	2.36E-03	5.20E-03	1.09E-01
C_2H_4	0.2526	0.5349	1.83E-01	4.03E-01	8.44E+00
C_2H_6	0.2770	0.5865	2.15E-01	4.74E-01	9.92E+00
C_3H_6	0.0772	0.1635	8.39E-02	1.85E-01	3.87E+00
C_3H_8	0.0219	0.0463	2.49E-02	5.49E-02	1.15E+00
C_4H_8	0.0246	0.0521	3.57E-02	7.86E-02	1.64E+00
C_4	0.0106	0.0225	1.60E-02	3.52E-02	7.35E-01
Benzene	0.0325	0.0688	6.55E-02	1.45E-01	3.02E+00
Toluene	0.0102	0.0216	2.43E-02	5.35E-02	1.12E+00
mXylene	0.0011	0.0023	2.98E-03	6.57E-03	1.37E-01
oXylene	0.0005	0.0011	1.42E-03	3.14E-03	6.57E-02
Ethyl Benzene	0.0004	0.0008	1.04E-03	2.28E-03	4.78E-02

Heating Value of Dry Make Gas	9890.2 kJ/kg (4252.0 Btu/lb) 10062.9 kJ/SCM (270.1 Btu/SCF)
Heating Value of Sweet Gas	26025.3 kJ/kg (11188.8 Btu/lb) 14499.1 kJ/SCM (389.2 Btu/SCF)

Table 24 Continued
WATER ANALYSIS

pH = 8.40

Species	C(mg/l)	Production Rate mg/hr	 lb/hr	g/kg Feed
NH_3	6149.00	1.51E+05	3.33E-01	6.9604
CL	20.00	4.91E+02	1.08E-03	0.0226
COD	6120.00	1.50E+05	3.31E-01	6.9275
CNO	367.00	9.01E+03	1.99E-02	0.4154
CN	56.20	1.38E+03	3.04E-03	0.0636
F	12.50	3.07E+02	6.77E-04	0.0141
N	6510.00	1.60E+05	3.52E-01	7.3690
S=	836.00	2.05E+04	4.53E-02	0.9463
SO_4	13.90	3.41E+02	7.53E-04	0.0157
SO_3	22.60	5.55E+02	1.22E-03	0.0256
SCN	361.00	8.87E+03	1.95E-02	0.4086

DESCRIPTION OF PROCESS STREAMS AND SAMPLING PROCEDURES

In order to achieve accurate data and good mass balance closures, great care must be taken that all instruments are properly calibrated and that good sampling and analysis techniques are used. This section presents a brief description of the various feed, effluent, and process streams, and how they are metered, controlled, sampled, and analyzed.

Coal Feed

Multiple samples of the feed are taken before each run, subjected to proximate and ultimate analyses, sieve analysis, and analyzed for several trace elements.

The feed stream is metered into the reactor by controlling the rate of revolution of the feed screw. The quantity of solid delivered per revolution of the screw has been remarkably constant, and thus the feed rate during the steady state portion of a run can be determined accurately.

Gas Feeds

The oxygen feed is from a bank of six cylinders; the nitrogen feed is from a six-thousand gallon liquid nitrogen tank with an atmospheric vaporizer; and the steam feed is from a high pressure building process steam line. All feed streams are preheated and metered, and are controlled by the process control computer system. The calibrations of the flow elements and transmitters are checked frequently.

Spent Char

Multiple samples are taken from the char receiver vessel or from the bottom of the reactor after a run. Analyses are essentially identical to those for the feed coal. The steady state char removal rate is determined from the total char removed, the total revolutions of the removal screw, and the rate of revolution of the screw during the steady state.

Cyclone Fines

Samples are collected from the cyclone solids collection tank. Analytical methods are the same as those for the feed coal.

Gas Samples

Gas samples are taken at operating pressure using one liter stainless steel bombs, and at lower pressures using one liter glass bombs. The glass bombs are coated internally with hexamethyldisilizane to reduce the adsorption of trace sulfur, nitrogen and hydrocarbon species. For the purposes of sampling, the steady state period is determined by the stability of various temperatures, pressures, flow rates, and levels over long periods of time.

Gas Samples from the PCS System--

Gases from the PCS system are metered and sampled after the final filter and before the dehydrators. Samples are collected at high pressure in stainless steel bombs, and at a lower pressure (approximately 20 psig) in glass bombs for later analysis by gas chromatography.

The reactor make gas flow meter-transmitter calibration is checked frequently, and the mass flow rate indicated by the data acquisition system is corrected for gas composition before being used for mass balances.

Gas Samples from the Sample Train--

In addition to the normal effluent streams, a small side stream is drawn off just downstream of the cyclone and passed through a sample train. For mass balances, the gas flow through the sample train is added to that metered at the PCS system outlet. During steady state operation, the gas flow through the sample train is metered with a test meter, and the water condensed in the train is measured and used as the primary measurement of the water content of the reactor make gas. Gas samples are taken in both stainless steel and glass bombs for GC analysis.

During a run, frequent gas samples are taken at the sample train and analyzed immediately on a Carle gas chromatograph as a means of following the course of the gasifier startup, and also as a means of evaluating steady state operation.

The gas sample train was designed to allow representative samples of particulates, tars, and condensed liquids to be taken. It is also necessary, especially in the case of trace element analysis, to trap all of the particulates, tars, and condensed liquids in one location to minimize sample contamination. For this purpose, a cold trap, which consists of a vertical stainless steel cylinder, equipped with gas inlet and exit ports, and a drain-plug to drain the condensed liquids, is installed in the sample train. The cylinder is loosely packed with stainless steel wool, which traps the particulates and tars as the gas travels through it. The entire trap is immersed in an ice bath. The liquid collected at the bottom of the cylinder is drained at the end of the run. When the gasifier reaches steady-state, the cold trap is opened and the sample-train gas is diverted through it for one hour. At the end of the run, the contents of the trap are separated into solid, tar, and liquid fractions, and analyzed.

ANALYTICAL PROCEDURES

Solids

Both proximate and ultimate analyses are performed on all solid input and output streams. The proximate analyses are performed using a Fisher Coal Analyzer Model 490. A Lindberg Combustion Furnace Model 123-SP is used to determine carbon and hydrogen for the ultimate analyses, and a Fisher Sulfur Analyzer Model 470 is used for sulfur analysis. Nitrogen is determined by the Kjeldahl-Gunning method, and oxygen is determined by difference. Certified coal standards are analyzed periodically to check the accuracy of all analyses.

Liquids

The liquids from the gasifier (water, tar, and oils) are analyzed for a wide variety of elements, ions, and chemical compounds. None of the results of these analyses are important to the mass balances or to the reactor modeling and will not be discussed here.

Gases

Hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, and hydrogen sulfide (in relatively high concentrations) are analyzed on a Carle Series SX AGC-111H gas chromatograph in conjunction with a Perkin-Elmer Sigma 10 Chromatography Data System. The AGC-111H is a dual valve, dual column, dual detector unit. Gases are injected through the first valve, which can also be switched for a column backflush. A second valve is located between the two columns and switches to align them in series or bypass flow to the second column. The first column is 6' x 1/8" 80% Poropak N and 20% Poropak Q. The second column is 7' x 1/4" Molecular Sieve 13X. A third column, 8% OV101 Chromasorb WAWDMCS, is used as a reference column. Columns are maintained at 75°C throughout the analyses.

Detection of all the above mentioned gases except hydrogen is performed with a thermal conductivity (TC) detector with helium carrier gas. Hydrogen is separated from the other gases by permeation through a palladium-tube transfer system. A second TC detector, using nitrogen carrier gas, detected H_2 at concentrations from 0.03% to 100%. The currents in both detectors are set at 20 mA. The Perkin-Elmer Sigma 10 Chromatography Data System performes automated valve switching and peak area integration.

Hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, carbon disulfide, and thiophene are analyzed on a Varian gas chromatograph. A gas sampling valve is added for sample injection. Sample components are separated on a 6' x 1/8" teflon 1.5% x E-60, 1% H_3PO_4 Carbopak B column which is temperature programmed. The column is held at 25°C for 3 minutes, heated to 130°C at 15°C per minute, and held at 130°C for 6 minutes.

Detection of sulfur gases in the high hydrocarbon coal matrix is accomplished using a Varian dual-flame flame photometric detector. The detector is heated to 180°C and helium is used as the carrier gas and hydrogen and air as flame gases.

Ethane, ethylene, all C3 and C4 hydrocarbons, and methanol are analyzed on a Tracor 550 gas chromatograph. A gas sampling valve and valve oven were added for sample injection. The sample components are separated on an 8' x 1/8" stainless steel Poropak Q column in series with an 10" x 1/8" stainless steel 20% Carbowax 20M TPA column. The columns are temperature programmed from 50°C to 200°C at 8°C per minute. The gases are detected by a flame ionization detector heated to 250°C. Helium is used as the carrier gas.

Benzene and toluene are analyzed on a Tracor 550 gas chromatograph with a heated gas sampling valve for injection. A 7' x 1/8" stainless steel 35% BC 150 Chromasorb PAW, DMCS column separates benzene and toluene. The column is temperature programmed from 120°C to 200°C at 8°C per minute. Components are detected by a flame ionization detector heated to 250°C. Helium is used as the carrier gas.

For all the gas chromatographic analyses, the Perkin-Elmer Sigma 10 Chromatography Data Station receives all detector outputs and integrates to calculate peak areas. The peak areas are converted to micromoles and mole % by external standard calibration curves in a series of steps using a Hewlett Packard 97 programmable calculator and the SAS statistical program. Final compilation and storage of data is accomplished by means of the GASS computer program described below.

GASS Computer Program--

GASS is an interactive data reduction system designed to process, log, and retrieve gas chromatography data, and to generate reports of gas analysis results. GASS routines are written in Applied Information Systems (AIS) PL/I.

An example of the output of the GASS program is given in Table 25 for the analysis of the 13:30 Sample Train gas sample from GO-84. Two replicate analyses are shown in the table. Also shown are the calibration curves used for the calculation of composition from peak areas. The percent recovery is calculated by totaling the micromoles calculated from the calibration curves and the peak areas, and dividing by the total micromoles injected from the gas sample loop.

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                         TABLE 25
              NCSU COAL GASIFICATION PROJECT
                    GAS CHROMATOGRAPHY
 CARLE           GAS   BOMB ANALYSIS         03/05/82

RUN NUMBER:  GO-84                  RUN DATE:  03/03/82
BOMB NUMBER:  28                    SAMPLE LOCATION:  S.TRAIN
SAMPLE TIME:  13:30                 ANALYST:  JO
DETECTOR:  TCD                      INSTRUMENT:  CARLE
T = 353K                            P =  5.00PSIG
LOOP SIZE =  1.00ML                 DILUTION FACTOR =  1.00

                  CALIBRATION CURVES USED:

  H2      6/29/81       .03< [A] <  7.00       r =  .993
  MIC-MOLES =  0.0000E+00*[A]**3 +  0.0000E+00*[A]**2 +
               4.1228E+00*[A]** 1.0000E+00 +  3.2626E-01

  CO2     12/22/81      .10< [A] < 54.00       r =  .999
  MIC-MOLES =  0.0000E+00*[A]**3 +  0.0000E+00*[A]**2 +
               4.0397E-01*[A]** 9.9500E-01 +  0.0000E+00

  CH4     01/19/81    1.00< [A] <  4.19       r =  .995
  MIC-MOLES =  0.0000E+00*[A]**3 +  0.0000E+00*[A]**2 +
               4.8577E-01*[A]** 1.0000E+00 + -1.8341E-02

  C2H4    10/20/81      .20< [A] <  3.00       r =  .999
  MIC-MOLES =  0.0000E+00*[A]**3 +  0.0000E+00*[A]**2 +
               4.2120E-01*[A]** 9.6900E-00 +  0.0000E+00

  C2H6    8/18/81       .50< [A] <  3.00       r =  .998
  MIC-MOLES =  0.0000E+00*[A]**3 +  0.0000E+00*[A]**2 +
               3.1330E-01*[A]** 1.0000E+00 +  1.8038E-02

  N2      6/30/81      1.70< [A] < 70.00       r =  .998
  MIC-MOLES =  0.0000E+00*[A]**3 +  0.0000E+00*[A]**2 +
               4.3745E-01*[A]** 1.0000E+00 + -5.4394E-01

  CO      6/30/81       .69< [A] < 60.00       r =  .994
  MIC-MOLES =  0.0000E+00*[A]**3 +  0.0000E+00*[A]**2 +
               4.4092E-01*[A]** 1.0000E+00 + -1.3328E-01

  H2S     8/19/81       .69< [A] <  2.00       r =  .998
  MIC-MOLES =  0.0000E+00*[A]**3 +  0.0000E+00*[A]**2 +
               3.6826E-01*[A]** 1.0000E+00 +  5.2120E-03
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                    TABLE 25 CONTINUED
                 GO-84           03/03/82
               BOMB NO. 28  GAS COMPOSITION
               S.TRAIN                13:30
                 SUMMATION ANALYSIS METHOD

     SAMPLE TYPE        AREA      MICROGRAM MOLES     MOLE PERCENTS

SAMPLE   1
   H2                  3.6235          15.2655            32.6884
   CO2                29.8073          11.8385            25.3501
   C2H4                 .5702            .2444              .5233
   C2H6                 .7286            .2463              .5274
   H2S                  .2420            .0943              .2019
   O2                   .0000            .0000              .0000
   N2                 20.8165           8.5622            18.3345
   CH4                 6.2607           3.0230             6.4732
   CO                 17.1436           7.4256            15.9007
       MICRO-MOLES INJECTED  46.2693
       PERCENT RECOVERY  100.93%

SAMPLE   2
   H2                  3.6704          15.4593            32.8915
   CO2                29.9288          11.8866            25.2901
   C2H4                 .5698            .2442              .5196
   C2H6                 .7296            .2466              .5247
   H2S                  .2417            .0942              .2005
   O2                   .0000            .0000              .0000
   N2                 20.8619           8.5821            18.2594
   CH4                 6.2716           3.0282             6.4429
   CO                 17.2204           7.4595            15.8709
       MICRO-MOLES INJECTED  46.2693
       PERCENT RECOVERY   101.58%

             STATISTICAL MOLE PERCENT ANALYSIS BOMB 28
             S.TRAIN                16:00       03/05/82

   GAS           MEAN        DEVIATION      +LIMIT         -LIMIT

   H2           32.7899        .1435        34.0799        31.5000
   CO2          25.3201        .0424        25.7014        24.9388
   C2H4           .5215        .0026          .5455          .4974
   C2H6           .5260        .0019          .5432          .5088
   H2S            .2012        .0010          .2104          .1920
   O2             .0000        .0000          .0000          .0000
   N2           18.2970        .0531        18.7740        17.8199
   CH4           6.4581        .0214         6.6504         6.2658
   CO           15.8858        .0210        16.0747        15.6969
```